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Structure-Miscibility Relationships in Weakly Interacting Polymer Blends

Theresa M. Hendrick

September 2012

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

Approved: _____
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Theresa M. Hendrick
September, 2012

Abstract

In the present research, the relationship between blend miscibility and constituent polymer structure was established. This work examines a series of blends of polyesters (PE's) and polycarbonates (PC's) having systematic variations in aliphatic and aromatic structural group content to establish how miscibility and phase behavior depend on polymer structure. The blends were prepared by solution blending and precipitating, while the polymer blend miscibility and phase behavior were characterized through differential scanning calorimetry (DSC). The glass transition temperatures (T_g) of the individual polymers and blends were measured. The polyesters and polycarbonates explored in this research were 4MC-PC (T_g = 135.2°C), BPA-TMC-PC 9371 (T_g = 213.4°C), Lexan 145 BPA-PC (T_g = 152.7°C), Teijin BPA-PC (T_g = 149.5°C), N-PC (T_g = 235.5°C), TCD-PC (T_g = 267.1°C), T(60)Az-N (T_g = 147.2°C), and T(80)Az-N (T_g = 74.8°C).

Generally, it was found that polycarbonate-polycarbonate blends were miscible, while polycarbonate-polyester and polyester-polyester blends were partially miscible at most. Of the 50:50 blends studied, the miscible blends were Lexan 145 BPA-PC and BPA-TMC-PC 9371, N-PC and BPA-TMC-PC 9371, TCD-PC and BPA-TMC-PC 9371, N-PC and Lexan 145 BPA-PC, and TCD-PC and N-PC. The partially miscible blends were T(80)Az-N blended with BPA-TMC-PC 9371, Lexan 145 BPA-PC, Teijin-PC, N-PC, TCD-PC, and T(60)Az-N. Other partially miscible blends included Teijin-PC and TCD-PC, and T(60)Az-N blended with BPA-TMC-PC 9371, N-PC, and TCD-PC. The blend that showed to be immiscible was T(60)Az-N and Lexan 145 BPA-PC. The results

showed that blends made up of two polycarbonates with similarities in aromatic and aliphatic group content brought about a miscible blend. For the PC-PE and PE-PE blends, those with more similar structural content were more miscible than those with less similar structural content.

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List of Abbreviations

PE – Polyester
PC – Polycarbonate
DSC – Differential Scanning Calorimetry
T_g – Glass Transition Temperature
HDT – Heat Distortion Temperature
SEM – Scanning Electron Microscopy
TEM – Transmission Electron Microscopy
IR – Infrared
NMR – Nuclear Magnetic Resonance
DMA – Dynamic Mechanical Analysis
ΔC_p – Specific Heat Increment
w – Weight Fraction
ΔG_m - Free Energy of Mixing
ΔH_m – Enthalpy of Mixing
T – Temperature
ΔS_m – Entropy of Mixing
R – Gas Constant
n – moles
 – Volume Fraction
x – Segments
χ – Flory-Huggins Polymer-Polymer Interaction Parameter
PVPh – Poly(vinylphenol)
BPA – Bisphenol-A
DCM – Dichloromethane
DMSO – Dimethyl sulfoxide
DMF – Dimethylformamide
i-PrOH – Isopropyl Alcohol
Diox – Dioxane
Acet – Acetone
MEK – Methyl Ethyl Ketone
PrOAc – n-Propylacetate
THF – Tetrahydrofuran
$CHCl_3$ – Chloroform
Tol – Toluene
M – Miscible
PM – Partially Miscible
IM – Immiscible
VSM – Very Slightly Miscible

1.0 Introduction

The present research explores the miscibility of polymer blends involving polycarbonates and polyesters (Figure 1 and Figure 2), each with differing structural content. It was proposed that blends with similar structural content will result in a miscible blend, and with increasing differences there may be less miscibility.

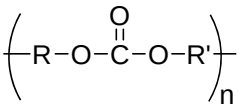


Figure 1. General Structure of Polycarbonate

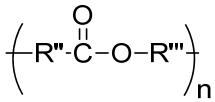


Figure 2. General Structure of Polyester

1.1 Polymer blends and their advantages

One main practical application of polymers is through the use of multicomponent polymer systems, such as polymer blends, and there are a variety of reasons to utilize them.[1] Polymer blends are physical mixtures of two or more polymers that do not have chemical bonding between them and have become a chief means for advancing and constructing polymeric materials.[2] A main reason polymer blends are used are to improve the chemical and physical properties of commercial polymers through the blending with other polymers.[3]

Some of the attractive features of polymer blends are that they can lower cost and add value. Polymer blends may result in an overall reduction of cost as a relatively inexpensive polymer can be added to a more expensive commercial polymer. The properties of polymers may also be enhanced with polymer blends. Properties that can be altered are heat distortion temperature (HDT), toughness, modulus, chemical resistance, and processability of the

commercial polymer to make it more ideal for a given application.[3] Also, polymer blends can be made in different compositions, and with differing compositions there are different properties that result. Lastly, polymer blends may be implemented more quickly and economically for a given application instead of looking into the chemistry of new polymers.

In addition, advantages to using polymer blends include impact modification when rubber is incorporated; improved environmental stress crack resistance; possible anti-slip, anti-block, and low coefficients of friction; and various commercial products can result from property compromise with elastomers. Some advantages of single phase blends include HDT enhancement, improved processability, plasticizer permanence, and no weld-line strength deterioration. Single phase blends also retain optical clarity, which is necessary in packaging and optical applications. Advantages to using two phase blends involve the ability to be used in rubber-toughened plastics, composites, and recycled polymer mixtures.[3] As it can be seen, the degree of miscibility of a blend can have either advantages or disadvantages depending on the application.

1.2 Methods to determine blend miscibility

There are various ways to determine polymer blend miscibility. One initial sign of possible miscibility is if the polymer solution is clear at high concentrations. While the results from this are not definitive, it is useful for examining potentially miscible blends. Other ways involve microscopy techniques such as optical, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Scattering methods are an option also with scattering techniques of light, x-ray, or neutron. Infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), dynamic mechanical analysis (DMA), and fluorescence may also be employed. A convenient and more reliable analysis technique is differential scanning

calorimetry (DSC). An important variable that results from the DSC analysis is the glass transition temperature (T_g) which helps determine phase behavior.

1.3 Glass transition temperature

The glass transition temperature is the temperature at which there is an onset of large scale segmental motion within a polymer. This transition is accompanied by more long-range motion of the chain, meaning more rotational freedom and more segmental motion. When this transition occurs, the space between the atoms, or the free volume, increases. Greater free volume of a polymer will prevent close packing and will therefore cause a lowering of the glass transition temperature. Therefore, polymers with larger groups that will hinder rotational freedom will have a higher T_g. The DSC trace shown in Figure 3 below is a basic example of what a glass transition looks like after the DSC analysis.[4] The transition is an "S" shaped curve. The analysis of this curve involves drawing a baseline where the curve begins and ends, and then a tangent line through the curve. Point A represents the onset of the T_g, the midpoint is represented by point B, and the point C represents the end point. Through using the DSC, the glass transition temperature helps to determine the phase behavior and miscibility of polymer blends.

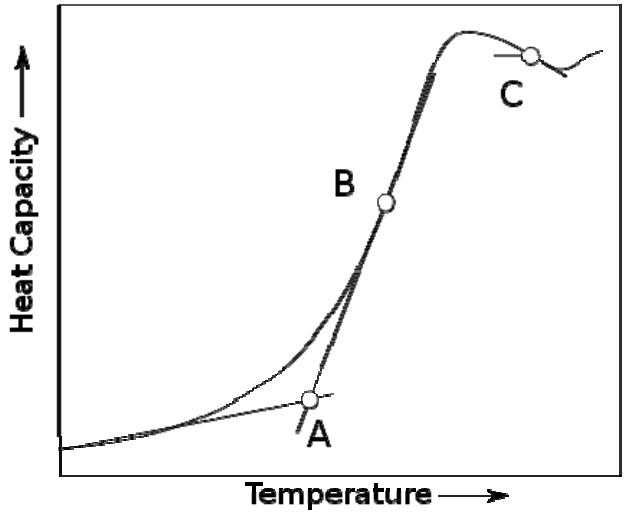


Figure 3. Basic DSC Trace Example

1.4 Phase behavior and miscibility of polymer blends

In the past it was thought that blend miscibility was rare, but now it is seen that different polymer blends can show varying behavior.[1] Polymer blends may form a single homogenous phase resulting in a miscible blend, or may phase separate resulting in an immiscible blend.[3] The phase behavior of polymer blends is primarily dependent on the extent of interactions between the constituent polymers, which is related to their structural group content.[5]

In general, blends can be classified into two general types, which are miscible and immiscible. A miscible blend is a single phase blend that has a high degree of homogeneity and exhibits intermolecular interactions, such as hydrogen bonding and Van der Waals forces, while an immiscible blend is a multiphase system that exhibits heterogeneous phase morphology.

1.5 Determining polymer blend miscibility through T_g

The phase behavior or miscibility of a blend can be determined from the glass transition behavior.[1] If a blend of polymers is completely miscible, there will be a single

glass transition temperature (T_g). If a blend is immiscible, there will be two distinct T_g's that are similar to those of the constituent polymers in the blend. There is also the possibility of a blend to not be fully miscible or immiscible, in which case it would be partially miscible. A partially miscible blend would exhibit two T_g's in between those of the constituent polymers, where one phase would be rich in one polymer and the second phase would be rich in the other.[6,7,8] When the composition of the blend is varied, the glass transition temperature of each polymer shifts as shown in Figure 4.[9] It can be seen that for a fully miscible blend, across all compositions there is a steady increase in the T_g and results in a plot with a slightly concave upward curve. For partially miscible blends there are two possible plots when the T_g is plotted versus composition. One is a curve that demonstrates two polymer rich phases at each extreme and with partial interaction in between. The other is a plot that demonstrates two polymer rich phases at each extreme, with no interaction taking place in between. The plot for the immiscible blend shows that there is no interaction between the polymers at all compositions. In addition to T_g, the specific heat increment (ΔC_p) has also been used to assess polymer blend behavior by DSC.[10,11]

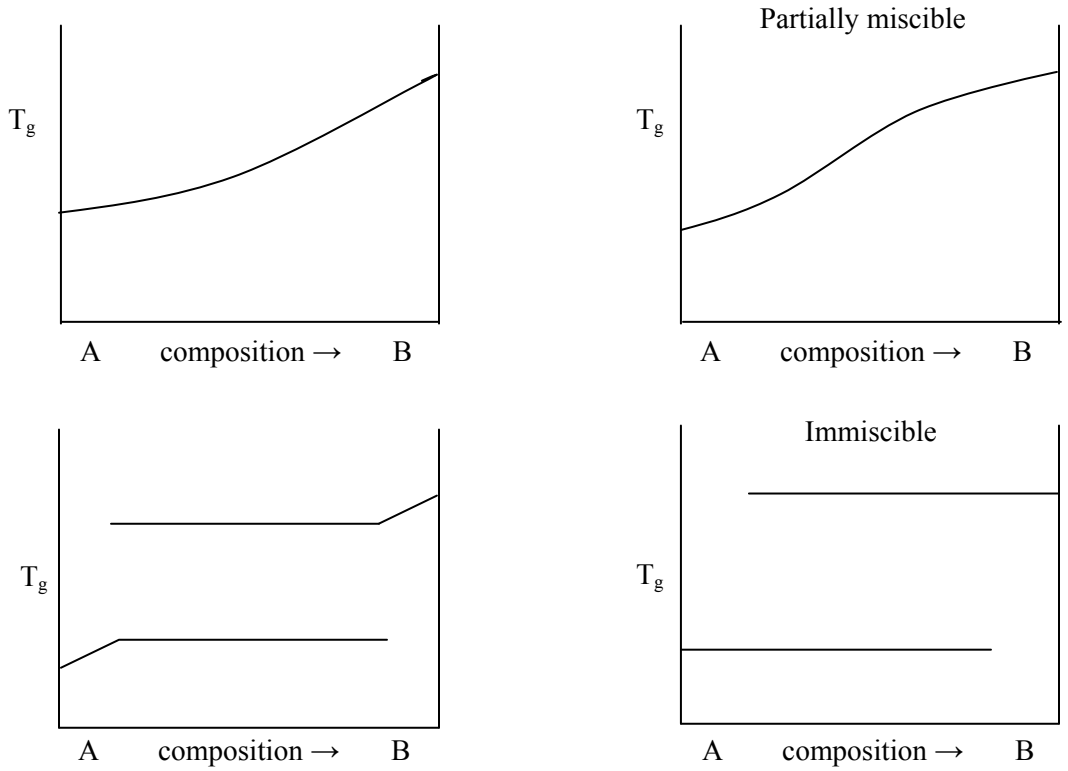


Figure 4. Glass Transition Temperature Behavior of Polymer Blends

1.6 The Fox and Couchman equations

The phase behavior of polymer blends can be examined by comparison of the measured T_g to a predicted or calculated T_g for the corresponding blend. [3,5] The glass transition temperature of blends can be calculated or predicted through the Fox equation and the Couchman equation, shown in Equations 1 and 2, respectively, where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are the glass transitions of the individual polymers, w_1 and w_2 are the weight fractions of the polymers in the blend, and ΔC_{p1} and ΔC_{p2} are the change in heat capacity of the polymers. When a polymer has a high ΔC_p it is possible that the T_g calculated from the Couchman equation will be slightly higher than the T_g from the Fox equation.[3]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad \text{Equation 1}$$

$$lnT_g = \frac{w_1 \Delta C_{p1} lnT_{g1} + w_2 \Delta C_{p2} lnT_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad \text{Equation 2}$$

The weight fractions of the polymer components in the system may also be calculated from the Fox and Couchman equations by rearranging them, which are shown in the Equations 3 and 4, respectively, where w_1' is the apparent weight fraction of polymer 1.[12,13] The weight fraction of polymer 2 can then be solved for by subtracting w_1' from 1. Knowing the weight fraction of each polymer present at a composition in a blend may also provide confirmation of the degree of miscibility of the blend. The most miscible blends will have experimental weight fractions the closest to the value from Fox or Couchman equation.

$$w_1' = \frac{T_{g1}(T_{g,b} - T_{g2})}{T_g(T_{g1} - T_{g2})} \quad \text{Equation 3}$$

$$w_1' = \frac{\Delta C_{p2}(lnT_g - lnT_{g2})}{\Delta C_{p1}(lnT_{g1} - lnT_g) + \Delta C_{p2}(lnT_g - lnT_{g2})} \quad \text{Equation 4}$$

1.7 Polymer blends thermodynamics

The best way to describe the degree of interaction of two polymers in a blend is through polymer blend thermodynamics, which is governed by the free energy of mixing, where ΔG_m is Gibb's free energy of mixing, ΔH_m is the enthalpy of mixing, T is temperature, and ΔS_m is the entropy of mixing (Equation 5).[3]

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{Equation 5}$$

In order for two polymers to be miscible, the free energy of mixing term must be negative, or less than zero. In order for the free energy of mixing to meet this criterion, there must be a degree of interaction between the polymers which will result in an exothermic or

favorable heat of mixing.[3] Unfavorable mixing occurs when ΔG_m is zero or positive, and this can happen when there are only van der Waals or dispersion forces present.[3]

There is an increase in the entropy of mixing for polymer blends, so the entropy term is always positive. The entropy term must exceed the enthalpy term in order to result in a negative free energy of mixing and a fully miscible blend. With blends made up of two dissimilar polymers, there will be a positive enthalpy term as they will have less attraction for each other and this is not favorable towards mixing.

There is a molecular weight effect on the miscibility of polymers. The entropy gain is larger with polymers of lower molecular weight, thereby promoting miscibility.[3] Also, a predetermined immiscible blend may be made miscible by chemical modification or by copolymerization as a means of getting favorable interactions.[2]

1.8 The Flory Huggins theory

In a polymer blend, two types of polymer chains may be considered to be comprised of segments within a lattice (Figure 5).[1] The two polymers that are shown represented by black and white circles each occupy a continuous sequence of segments. There may be interactions between segments of the two different polymers or even interactions within the same polymer when in a blend, which will affect the miscibility; and the Flory-Huggins theory, another theory of polymer blend thermodynamics that takes these interactions into account.[1]

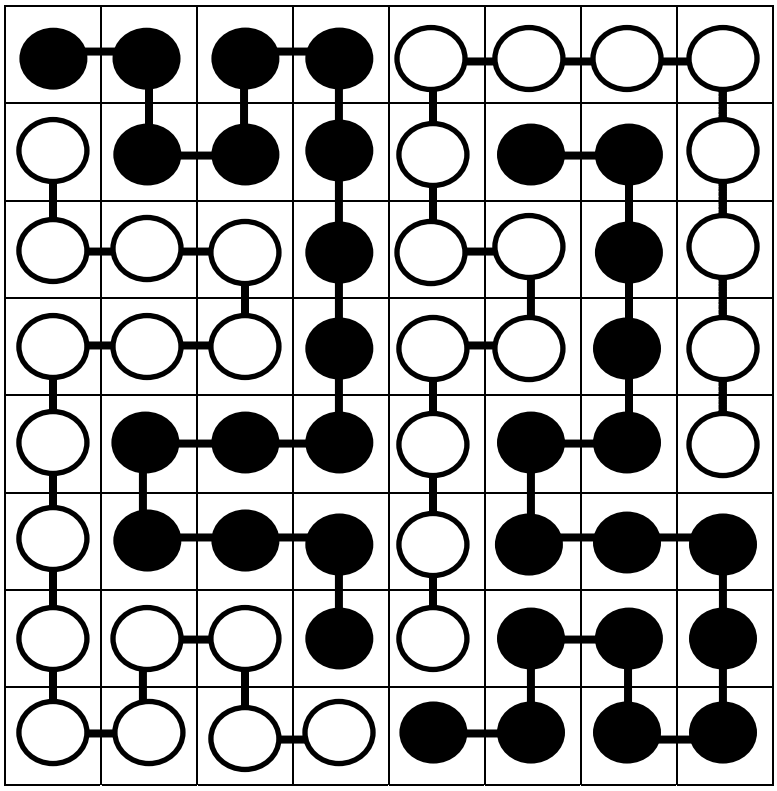


Figure 5. Polymer Chains as Segments in a Blend

The Flory-Huggins equation for the Gibbs free energy of mixing for polymer blends is shown below, where R is the gas constant, T is temperature, n_1 and n_2 are the number of moles of polymer 1 and polymer 2, □$_1$ and □$_2$ are the volume fractions of the polymers, x_1 is the segments occupied by polymer 1, and $\mathcal{X}$ is the Flory-Huggins polymer-polymer interaction parameter (Equation 6).

$$\Delta G_m = RT[\underbrace{n_1 ln\emptyset_1 + n_2 ln\emptyset_2}_{\text{Combinatorial entropy of mixing}} + \underbrace{x_1 n_1 \emptyset_2 \mathcal{X}}_{\text{Enthalpy term}}] \qquad \text{Equation 6}$$

The combinatorial entropy of mixing is comprised of the first two terms on the right hand side of the equation and the enthalpy term is comprised of the third term in the equation. The entropy term represents how the polymers fit into the lattice, while the enthalpy term represents the interactions between the polymers within the lattice.

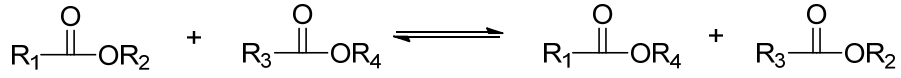
In polymers, atoms are restricted by being tied into a polymer chain which means that the mixing is much less random and the entropy gain is much lower. Therefore, the entropy term is not sufficient enough to bring about a fully miscible blend between two polymers and the enthalpy term then becomes the dominant term.[1]

1.9 Preparing polymer blends

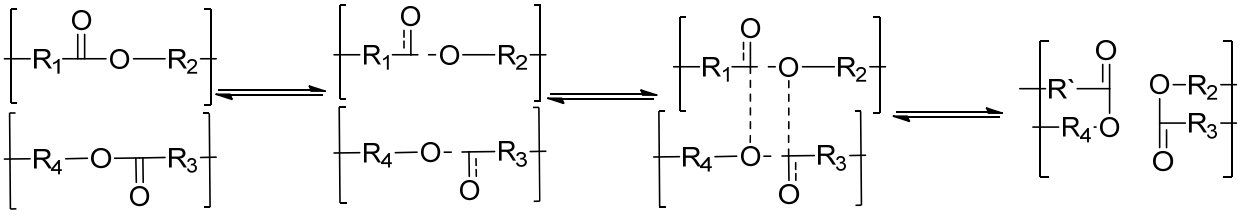
Polymer blends can be prepared in a variety of ways, two of which are solution mixing and melt mixing. In solution mixing, polymers are dissolved individually into a common solvent, are combined in the necessary ratios, are precipitated into a non-solvent, and are then dried. In melt mixing, polymers (in pellet form) are mixed in the molten state. Solution mixing was chosen over melt mixing for this current research because melt mixing is a much larger scale process and involves polymers being held at higher temperatures for an extended period of time which makes it possible for chemical changes to occur.

1.10 Interchange reactions

Often when held at high temperatures for extended periods of time, blends comprised of two polyesters undergo interchange reactions where either ester group in the polymer chain or end-group reacts (Scheme 1 and Scheme 2).[14,15,16]



Scheme 1. Ester Interchange



Scheme 2. Associative reaction mechanism for the ester interchange of polyesters[17]

There is a similar reaction that can occur between a blend of a polycarbonate and polyester (PC-PE).[16,18] This results in the altering of the chemical nature of the final product as it becomes a random copolymer.[14] In the case of PE-PC blends, decarboxylation can occur.[19] This resulting blend would be miscible and have a single T_g, have a significantly lowered melting temperature, and would not demonstrate any crystalline behavior.[19,20] The blends in the current study were prepared and characterized with minimal thermal history to exclude the potential of any transesterification as much as possible.

1.11 Previous work on strongly interacting polymer blends

When two chemically different polymers are blended they can undergo phase separation and two separate phases are formed; this is mainly dependent on the degree of interaction between the constituent polymers determined by their structural content.[1,5] Blends that are strongly interacting have hydrogen bonding intramolecular forces present between the two polymers of the blend, while weakly interacting blends do not have hydrogen bonding. When studying the miscibility of poly(vinylphenol) (PVPh) with polyesters, Landry and coworkers assert that the balance of aromatic and aliphatic character will determine the miscibility of a blend.[3] From their work, it was determined that the copolyesters derived from aliphatic diols were more miscible with PVPh than the copolyesters derived from aromatic diols.

Massa, et al. found that polymer architecture, chemical structure, and interactions affect polymer blend miscibility in blends of linear polymers with hyperbranched polymers. These combinations resulted in multi-phase blends.[5] There was potential for hydrogen bonding between the polymers; however there were not ample intermolecular interactions to overcome the chemical and architectural differences between the two different polymers.

1.12 Weakly interacting blends of polycarbonates and polyesters

The blends explored in this present study are comprised of polycarbonates and polyesters. PC's are used in the engineering thermoplastics industry because their properties allow for high HDT and have an exceptional balance of toughness and rigidity. However, PC's lack stress crack resistance to various chemicals, which can be improved by blending with polyesters.[21] Bisphenol-A polycarbonates (BPA-PC) are commercially important when blended with PE's when making high performance plastics.[22]

1.13 Previous work on weakly interacting PC-PE blends

Particular polymers explored in the present research have also been studied by other groups in terms of miscibility of various blends. Research done by Yang and Yetter explored the miscibility of a polyester, T(40)Az-N, with two BPA-PC's having different molecular weight (Figure 6 and Figure 7).[21] The polyester studied was a poly[4,4'-(2-norbornylidene)diphenol-co-(60%)terephthalic acid/(40%)azelaic acid], or T(40)Az-N, while the polymers explored in the present research are T(60)Az-N and T(80)Az-N. The T(40)Az-N is more aromatic and less aliphatic than the T(60)Az-N and T(80)Az-N in that the ratio of terephthalic acid to azelaic acid is 0.6:0.4, while the ratios for T(60)Az-N and T(80)Az-N are 0.4:0.6 and 0.2:0.8, respectively. The polycarbonates that the T(40)Az-N was mixed with were Lexan 145 BPA-PC and Makrolon, which has the same structure as Lexan 145 BPA-PC and is just a higher molecular weight polymer.

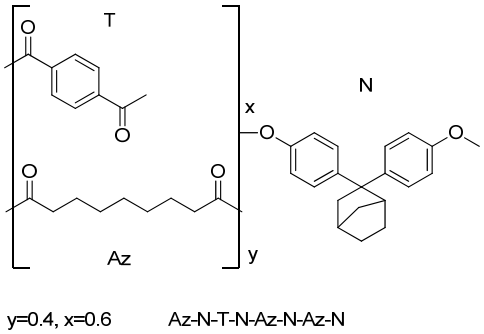


Figure 6. Structure of T(40)Az-N

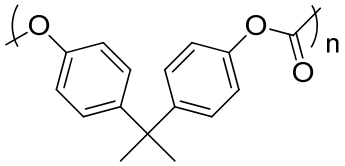


Figure 7. Structure of BPA-PC

Yang and Yetter's results showed that the polyester T(40)Az-N was miscible with the lower molecular weight Lexan 145 BPA-PC at all compositions and exhibited a single T_g; however it was not miscible with the higher molecular weight BPA-PC, Makrolon, as it had two T_g's for most compositions. This supports the theory that a lower molecular weight polymer promotes miscibility. Apart from the low molecular weight, the miscibility of the T(40)Az-N with Lexan 145 BPA-PC could be attributed to the balance of aliphatic and aromatic moieties between the structures, with both having more aromatic character than aliphatic character.

Yang and Yetter's work is also consistent with previous work by Cruz, Paul, Barlow, et al., on blends of BPA-PC with aliphatic polyesters. Paul's group found that poly(ε-caprolactone) is miscible in all proportions with BPA-PC.[23] Further, other linear aliphatic polyesters having a CH_2/COO ratio of 2 to 5 are miscible with BPA-PC, ratios up to 7 are partially miscible, and ratios over 7 are immiscible.[24,25] Methyl-substituted aliphatic polyesters showed different behavior and were much less miscible. These results could be

explained by the heats of mixing of non-polymer analogs of BPA and the aliphatic polyesters, as well as by the binary interaction model later developed.[25,26,27] Based on these results, it was anticipated that the degree of aliphatic character could influence the blend miscibility in the current study of polycarbonates and polyesters that vary in aliphatic and aromatic character.

Paul and Haggard studied effects of polymer structure on miscibility with blends of BPA-TMC-PC 9371 (Figure 8) and BPA-PC.[28] BPA-TMC-PC 9371 is a polymer based on BPA and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane and is an amorphous material with high heat resistance.[29] Apart from thermal properties, Paul and Haggard also analyzed the mechanical properties of BPA-TMC-PC 9371 along with BPA-PC. BPA-TMC-PC 9371 has a high T_g, tensile modulus, and yield stress, but has a low elongation at break. When it was blended with the BPA-PC (which has a high elongation at break) the elongation at break was reduced upon the addition of BPA-TMC-PC 9371, but the modulus and yield stress were increased.

Figure 8. Structure of BPA-TMC-PC 9371

The blend of BPA-TMC-PC 9371 and BPA-PC resulted in a single phase blend with a single T_g when analyzed by DSC. The formation of a miscible blend between the two PC's suggests that there were favorable interactions or that the entropy of mixing offset any unfavorable interactions that were present. It was also discovered that interchange reactions

could have taken place between two polycarbonates in a blend when held at high temperatures. Paul and Haggard were able to confirm whether or not this took place by redissolving and recasting the blends. If there was a single phase that resulted, it indicated a permanent change in the phase behavior because of the interchange reaction. However, if there was still phase separation no reaction occurred. Paul and Haggard concluded that precipitation into methanol gave the true miscibility of the blend, and that transesterification was not the determining factor in miscibility when the thermal history consisted only of ordinary DSC analysis.

Given the previous work done on weakly interacting polycarbonate and polyester blends, it is proposed that there will be greater miscibility between blends with similar ratios of aliphatic and aromatic content. Also, it is expected that with increasing differences in structural content there will be less miscibility.

2.0 Experimental

2.1 Materials

All polymers and chemicals were used as received without any further purification.

Methanol was purchased from Fisher Scientific and dichloromethane was purchased from Macron Chemicals. All solvents used in sample preparation and solubility testing were of ACS certified purity grade.

4MC-PC, BPA-TMC-PC 9371, Lexan 145 BPA-PC, Teijin-PC, N-PC, TCD-PC, T(60)Az-N, and T(80)Az-N were generously donated by Eastman Kodak.

2.2 Instrumentation

Glass transition temperature data were obtained using a Perkin Elmer Diamond DSC and a TA Instruments DSC 2010, both cooled by liquid nitrogen. A temperature calibration was performed with an indium sample, and the instrument calibration was adjusted to be within 0.05°C of the indium melting point, 156.60°C. All samples were prepared in a capped but not hermetically sealed aluminum pan. All samples followed a several-step analysis process that consisted of at least two heating cycles according to the typical process shown below. Typically, the final heating temperature would be 50°C higher than the highest T_g of the blended polymers, but no more than 300°C as this is the highest temperature the instrument is capable of reaching. After each heating and cooling cycle, the temperature was held for 0.1 and 5 minutes, respectively. The onset, midpoint, endpoint, and ΔC_p of all glass transition temperatures were reported. The process shown below was used for the TCD-PC polymer and its corresponding blends.

Step 1 – Heat to 300°C at 20°C/min

Step 2 – Hold at 300°C for 0.1 min

Step 3 – Cool to 20°C at 320°C/min

Step 4 – Hold at 20°C for 5.0 min

Step 5 – Reheat to 300°C at 20°C/min

2.3 Blend preparation

Blends were prepared by solution blending and precipitating into methanol, following the methods of other blends preparations.[3,21] 5% polymer in dichloromethane solutions were prepared (0.125g/2.5mL) and were allowed to stir for an hour. Dichloromethane was a suitable solvent for every polymer except for the T(80)Az-N polymer which was prepared in a 50:50 mixture of THF and dichloromethane. This solvent mixture was discovered by performing a solubility test on this polymer.

For 50:50 blends, equal volumes of two different polymer solutions were mixed with stirring. This solution was then precipitated by slowly adding it to 150 mL of methanol, the non-solvent, with stirring. The solution was suction filtered to obtain a white precipitate. The polycarbonate and polyester blend materials were allowed to air dry on a watch glass overnight and were then transferred to a scintillation vial and placed in a vacuum oven to dry for approximately 48 hours at a temperature no higher than 70°C. The temperature was not allowed to exceed 70°C so it would not reach the glass transition temperature of some of the material it was drying.

For 25:75 blends, the same procedure was followed except 2.5 mL of one 5% polymer solution was mixed with 7.5 mL of the other 5% polymer solution. The 50:50

blends were considered first to determine the general extent of miscibility. From these results, other compositions of chosen blends were examined. When blending a polymer with a BPA-PC polymer, it was first blended with the lower molecular weight Teijin-PC, the reasoning being that if there were no signs of miscibility with the lower molecular BPA-PC, Teijin-PC, there would not be miscibility with the higher molecular weight Lexan 145 BPA-PC. Table 1 shows the 50:50 polymer blends that were prepared and Table 2 shows the 25:75 polymer blends that were prepared. Some of the same blends were prepared in a 75:25 ratio to complete the series.

Table 1. 50:50 Polymer Blends

	Polymer 1 (50%)	Polymer 2 (50%)
Blend 1	T(80)Az-N	BPA-TMC-PC 9371
Blend 2	T(80)Az-N	Lexan 145 BPA-PC
Blend 3	T(80)Az-N	N-PC
Blend 4	4MC-PC	Teijin-PC
Blend 5	T(80)Az-N	T(60)Az-N
Blend 6	Lexan 145 BPA-PC	BPA-TMC-PC 9371
Blend 7	4MC-PC	BPA-TMC-PC 9371
Blend 8	T(60)Az-N	BPA-TMC-PC 9371
Blend 9	N-PC	BPA-TMC-PC 9371
Blend 10	T(60)Az-N	Lexan 145 BPA-PC
Blend 11	Lexan 145 BPA-PC	N-PC
Blend 12	T(80)Az-N	Teijin-PC
Blend 13	T(60)Az-N	TCD-PC
Blend 14	T(60)Az-N	N-PC
Blend 15	TCD-PC	N-PC
Blend 16	TCD-PC	Teijin-PC
Blend 17	TCD-PC	T(80)Az-N
Blend 18	TCD-PC	BPA-TMC-PC 9371

Table 2. 25:75 Series Polymer Blends

	Polymer 1 (25%)	Polymer 2 (75%)
Blend 19	BPA-TMC-PC 9371	Lexan 145
Blend 20	Lexan 145	BPA-TMC-PC 9371
Blend 21	N-PC	Lexan 145
Blend 22	Lexan 145	N-PC
Blend 23	TCD-PC	Teijin-PC
Blend 24	Teijin-PC	TCD-PC

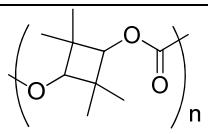
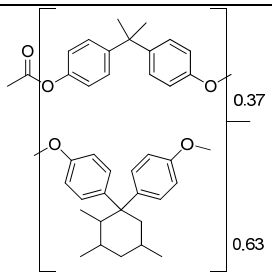
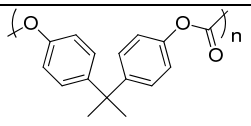
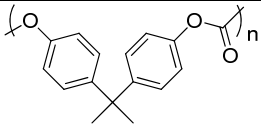
2.4 Solubility test – T(80)Az-N

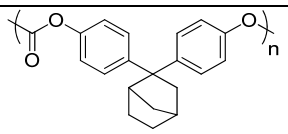
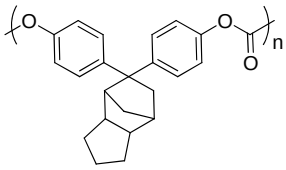
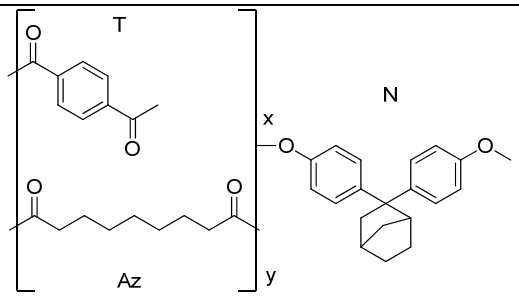
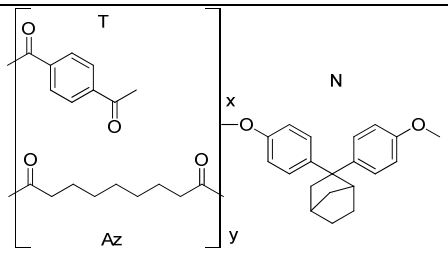
5% polymer solutions of T(80)Az-N (0.25g) in 5mL of various solvents were prepared. The polymer was added to the solvents with stirring and was allowed to stir for an hour. The solvents used were acrylonitrile, dimethyl sulfoxide, dimethylformamide, isopropanol, dioxane, acetone, methyl ethyl ketone, n-propyl acetate, tetrahydrofuran, chloroform, toluene, and dichloromethane.

3.0 Results and Discussion

Various types of polycarbonates and polyesters can be blended together in order to obtain more ideal thermal properties than those of the individual polymers themselves. The objective of the present research is to explore how the structural content of polycarbonates and polyesters affects the thermal properties of the polymer blends through looking at the glass transition temperature. It is expected that blends with similar structural content will result in a miscible blend, and with increasing differences there may be less miscibility. The structures of the polycarbonates and polyesters explored in this study are shown in Table 3.

Table 3. Structures of Polycarbonates and Polyesters

Polymer	Structure
4MC-PC	
BPA-TMC-PC 9371	
Lexan 145 BPA-PC	
Teijin-PC (low MW BPA-PC)	

N-PC	
TCD-PC	
T(60)Az-N	 y=0.6, x=0.4 Az-N-T-N-Az-N-Az-N
T(80)Az-N	 y=0.8, x=0.2 Az-N-T-N-Az-N-Az-N

3.1 Polycarbonate and polyester structural makeup

The polycarbonates used were 4MC-PC, BPA-TMC-PC 9371, Lexan 145 BPA-PC, Teijin-PC, N-PC, and TCD-PC. In their structure content, they all contain carbonate groups (-O-(C=O)-O); however they differ in the rest of their chemical make-up. 4MC-PC is a polycarbonate of 1,4-dioxy-2,2,4,4-tetramethylcyclobutane and is the only polycarbonate

with complete aliphatic character as it is made up of a cyclobutane and four methyl groups. BPA-TMC-PC 9371, N-PC, and TCD-PC all have a mix of aliphatic and aromatic character. The BPA-TMC-PC 9371 is a copolycarbonate based on bisphenol-A and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane. This is believed to be a random copolymer and is made up of 37% of the BPA monomer and 63% the TMC monomer. The overall structure of the TMC portion contains two benzene rings as well as a saturated trimethylcyclohexanone ring. The BPA portion contains two benzene rings and an isopropylidene group. N-PC is a poly(oxycarbonyloxy-1,4-phenylene-norbornylidene-1,4-phenylene) and has two benzene rings as well as a saturated bridged cyclohexane ring. TCD-PC is a poly(oxycarbonyloxy-1,4-phenylene-tricyclodecylidene-1,4-phenylene). The structure of TCD-PC is made up of two benzene rings contributing to its aromatic character as well as a saturated bridged cyclohexane and a cyclopentane which contribute to its aliphatic character. Lexan 145 BPA-PC and Teijin-PC have the same structural make up. Teijin-PC is a lower molecular weight polymer than Lexan 145 BPA-PC. They are a poly(oxycarbonyloxy-1,4-phenylene-isopropylidene-1,4-phenylene) and have a mix of saturated and unsaturated structural content due to the two aromatic rings and an isopropylidene group.

The polyesters explored in this study were T(60)Az-N and T(80)Az-N. The T(60)Az-N is a poly[4,4'-(2-norbornylidene)diphenyl-co-(40%)terephthalic acid/(60%)azelaic acid] and T(80)Az-N is the same polymer, except with 20% terephthalic acid and 80% azelaic acid. T(60)Az-N and T(80)Az-N can be synthesized by the condensation polymerization of 4,4'-(2-norbornylidene)diphenol and terephthalic acid/azelaic acid chlorides with a 40/60 or 20/80 molar ratio, respectively. These polyesters are random copolymers because although

every other unit is N, whether the next unit is a T or Az is random. Both exhibit aliphatic and aromatic character. The T portion comes from terephthalic acid and is aromatic, the Az portion comes from azelaic acid and is aliphatic bearing seven methylene groups between the two carbonyls, and the N portion comes from norbornylidene and is both aromatic and aliphatic. The only difference between the two polyesters is the ratio of T:Az.

3.2 Polymer blend preparation results

There are a variety of methods to prepare polymer blends. The blends in this study were prepared by solution blending and precipitation. Polymers were dissolved in dichloromethane and a clear solution was obtained, which is required in order to have proper homogenous blending in the next step. All polymers were fully miscible in dichloromethane, except T(80)Az-N. Dichloromethane was chosen as the main solvent due to its compatibility with the polymer samples and its low boiling point allowing for easy removal from the polymer samples.

To prepare the blends, two of the individually dissolved polymers were combined and a clear solution was obtained in all instances. The combined solution was precipitated dropwise in methanol and, upon addition, the blended polymers immediately precipitated out and a cloudy solution resulted. Methanol was used to precipitate the blends because it is a low boiling solvent that all polymers were insoluble in and that could be easily removed from the samples. This was followed by suction filtration and the precipitate was dried in a 70°C vacuum oven for approximately 48 hours to ensure the blends were sufficiently free of solvent. The precipitates ranged from white powders to a white netted material.

3.3 Solubility test results for T(80)Az-N

A solubility test was performed on the T(80)Az-N polyester to determine if there was a more ideal solvent to use for the solution blending. Along with dichloromethane (DCM), the other different solvents tested on T(80)Az-N were dimethylsulfoxide (DMSO), dimethylformamide (DMF), isopropyl alcohol (i-PrOH), dioxane (Diox), acetone (Acet), methylethyl ketone (MEK), n-propylacetate (PrOAc), tetrahydrofuran (THF), chloroform ($CHCl_3$), and toluene (Tol). The results of the solubility test are shown in a Wiehe 2-dimensional solubility parameter plot (Figure 9).[30] Solvents were rated on a scale from 1 to 6, with 1 being the most soluble and 6 being the least soluble. $CHCl_3$ (1), THF (1), Diox (1), and DMF (1) were the best solvents for T(80)Az-N. The less ideal solvents were DMSO (2), MEK (2.5), PrOAc (2.5), Acet (3), Tol (3), and DCM (3). i-PrOH (6) was the worst solvent. It was found that THF was the most ideal solvent to use due to its lower boiling point compared to DIOX and DMF and its lower toxicity than $CHCl_3$. T(80)Az-N was tested in a 50/50 solution of THF and dichloromethane so that there would be a greater ratio of DCM to THF in the overall blend. This produced a clear solution ensuring that the polymer was soluble.

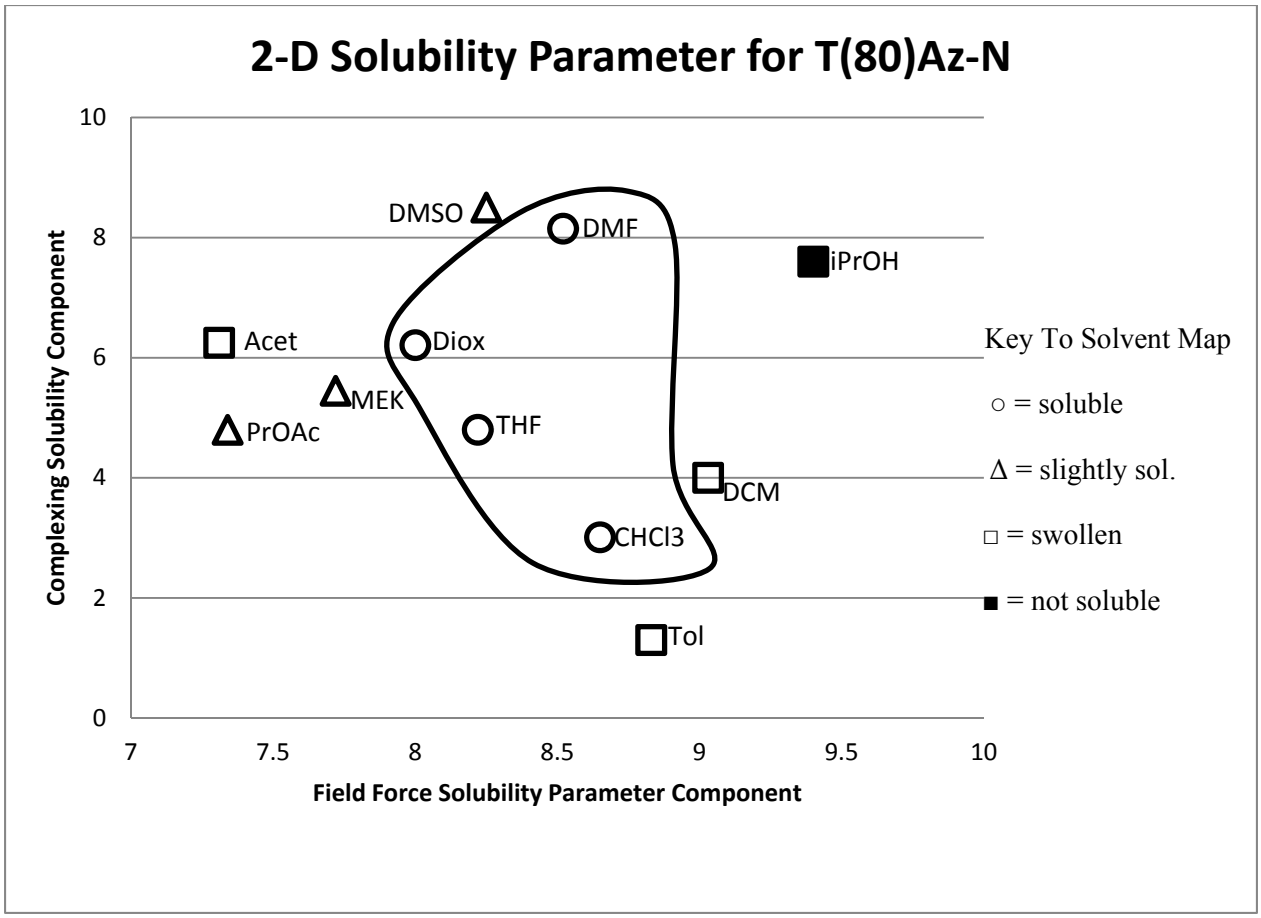


Figure 9. Wiehe 2-Dimensional Solubility Parameter Plot

3.4 Thermal analysis of polymers and blends

The individual polymers and blends were analyzed by differential scanning calorimetry (DSC). Samples (10 mg-15 mg) were sealed in aluminum pans and followed a sequence of heating, cooling, and isothermal steps. There were at least two heating cycles performed so that the sample would have a thermal history and the samples were heated to at least 50°C higher than the expected T_g of the polymer, but no higher than 300°C. The onset, midpoint, endpoint, and ΔC_p for all individual polymers are shown in Table 4 and the subsequent DSC spectra for each polymer is shown in the Appendix in Figures 18-25. The midpoint is the reported value, but the onset and endpoint T_g's were looked at in order to determine how broad the transition was. A very broad transition would mean that there

would be a lower degree of homogeneity in the polymer blend. Although the T_g data are reported to the second decimal place for computational purposes, the T_g values measured are uncertain to $\pm$ 0.2°C, and the ΔC_p values are uncertain to $\pm$ 0.02 J/g°C. For the blends the uncertainty in ΔC_p is estimated to be $\pm$ 20%.

Table 4. DSC Data for Polymers

	T_g (°C)			
Sample	Onset	Mid	End	ΔCp
4MC-PC	115.36	135.18	142.69	0.12
BPA-TMC-PC 9371	207.50	213.39	217.65	0.16
Lexan 145 BPA-PC	150.41	152.71	154.71	0.19
Teijin-PC	145.99	149.48	151.90	0.20
N-PC	223.12	235.50	241.83	0.16
TCD-PC	261.92	267.11	270.48	0.20
T(60)Az-N	138.08	147.17	155.44	0.22
T(80)Az-N	73.25	74.84	76.56	0.03

Based on the above T_g values for the individual polymers, the 50:50 polymer blends were analyzed by DSC in a similar method. There were PC-PC blends, PC-PE, and PE-PE blends studied. The samples underwent at least two heating cycles and were heated to at least 50°C higher than the polymer with the highest T_g to ensure that a wide enough temperature range in which a T_g could potentially occur in would be analyzed. The onset, midpoint, endpoint, ΔC_p, and calculated Fox T_g for all polymer blends are shown in Table 5. Some blends exhibited two T_g's, a lower and higher one, each represented with an L and H, respectively. It is necessary to know the Fox T_g in order to determine the degree of miscibility of the blend. The proximity of the measured T_g to the calculated Fox T_g will determine this.

Table 5. DSC Data for Polymer Blends

Blend	Polymer 1	Polymer 2	Onset (°C)	Midpoint (°C)	Endpoint (°C)	ΔC_p	Fox Tg (°C)
1	T(80)Az-N	BPA-TMC-PC 9371	157.65	163.81	171.57	0.22	132.62
2L	T(80)Az-N	Lexan 145	73.26	74.95	77.34	0.03	109.86
2H	T(80)Az-N	Lexan 145	120.83	133.25	142.18	0.34	
3L	T(80)Az-N	N-PC	69.58	94.34	119.77	0.07	140.10
3H	T(80)Az-N	N-PC	168.86	177.67	188.05	0.13	
4	4MC-PC	Teijin-PC	143.84	149.73	153.07	0.10	142.25
5	T(80)Az-N	T(60)Az-N	124.59	133.49	142.97	0.20	107.60
6	Lexan 145	BPA-TMC-PC 9371	180.02	181.36	182.54	0.07	181.03
7L	4MC-PC	BPA-TMC-PC 9371	115.71	123.14	127.42	0.05	170.87
7H	4MC-PC	BPA-TMC-PC 9371	205.98	209.28	211.14	0.06	
8L	T(60)Az-N	BPA-TMC-PC 9371	130.90	141.48	153.00	0.05	177.86
8H	T(60)Az-N	BPA-TMC-PC 9371	173.40	182.99	188.00	0.11	
9	N-PC	BPA-TMC-PC 9371	211.90	219.82	224.86	0.16	224.20
10L	T(60)Az-N	Lexan 145	140.14	143.49	148.16	0.05	149.92
10H	T(60)Az-N	Lexan 145	149.13	153.94	155.54	0.10	
11	Lexan 145	N-PC	178.04	186.59	194.40	0.16	190.44
12L	T(80)Az-N	Teijin-PC	126.44	132.47	138.04	0.12	108.59
12H	T(80)Az-N	Teijin-PC	151.54	157.74	161.10	0.01	
13	T(60)Az-N	TCD-PC	188.71	195.00	203.96	0.10	199.65
14	T(60)Az-N	N-PC	174.08	212.53	234.08	0.23	187.14
15	TCD-PC	N-PC	244.00	249.37	254.00	0.16	250.83
16L	TCD-PC	Teijin-PC	183.08	190.69	198.82	0.18	201.17
16H	TCD-PC	Teijin-PC	225.72	233.99	240.74	0.08	
17L	TCD-PC	T(80)Az-N	176.08	184.38	191.53	0.17	150.17
17H	TCD-PC	T(80)Az-N	221.80	230.21	238.60	0.08	
18	TCD-PC	BPA-TMC-PC 9371	221.40	231.71	241.76	0.16	238.84

3.5 Miscibility of 50:50 polymer blends

There was a general criterion followed for determining the degree of miscibility of the polymer blends. In order for a blend to be classified as miscible (M), it would have to demonstrate a single T_g within a few degrees of the calculated T_g from the Fox equation. There are two different possible criteria for a blend to be partially miscible (PM). The blend would have two T_g's that were intermediate between the constituent T_g's, or would have one T_g intermediate between the constituent T_g's which would be substantially different from the

Fox equation T_g. This second criterion was to account for the lack of resolution of the second T_g by DSC that often occurs in polymer blends. A blend was classified as immiscible (IM) if there were two T_g's very close to the T_g's of each polymer in the blend. In the case that a blend was very slightly miscible (VSM), the glass transition behavior would be somewhere between PM and IM. The miscibility results are summarized in Table 6.

Table 6. Miscibility Results of Polymer Blends

	T(80)Az-N	BPA-TMC 9371	Lexan 145	Teijin-PC	N-PC	4MC-PC	T(60)Az-N	TCD-PC
T(80)Az-N		PM	PM	PM	PM		PM	PM
BPA-TMC 9371	PM		M		M	VSM	PM	M
Lexan 145	PM	M			M		IM	
Teijin-PC	PM					IM		PM
N-PC	PM	M	M				PM	M
4MC-PC		VSM		IM				
T(60)Az-N	PM	PM	IM		PM			PM
TCD-PC	PM	M		PM	M		PM	

3.6 Fully miscible PC-PC blends

Out of the 18 blends explored in this study, five were fully miscible and all were PC-PC blends. BPA-TMC-PC 9371 and Lexan 145 BPA-PC were fully miscible. This blend exhibited a single T_g at 181.36°C, which is only 0.33°C higher than the calculated Fox T_g of 181.03°C. These two polymers have similar structural content since both have aromatic and aliphatic moieties. The BPA-TMC-PC 9371 is a copolymer that is made up of a BPA group and a TMC group, while Lexan 145 BPA-PC is a bisphenol-A. The similarity of both having a BPA group and a similar enough ratio of aliphatic and aromatic character in both structures is why this blend was fully miscible. This result agrees with Paul and Haggard's work as their work also resulted in a miscible blend between BPA-TMC-PC 9371 and a BPA-PC.[28]

BPA-TMC-PC 9371 and N-PC was a fully miscible blend which had a single glass transition at 219.82°C which is just a few degrees lower than 224.20°C, which is the Fox T_g. These two polymers both have aromatic and aliphatic group content. The TMC portion of the copolymer BPA-TMC-PC 9371 has aliphatic character due to the trimethyl substituted cyclohexane ring and aromatic character from the two benzene rings. N-PC has a similar structure in that it has an aliphatic norbornylidene ring in between two aromatic benzene rings. This similarity in structural content from a similar ratio of aromatic and aliphatic content brought about a fully miscible blend.

Another fully miscible blend was BPA-TMC-PC 9371 and TCD-PC. This blend had a single T_g at 231.71°C, which is in close proximity to the Fox T_g of 238.84°C. The tricyclodecane ring system in the TCD-PC is highly aliphatic, as is the trimethyl substituted cyclohexane in the BPA-TMC-PC 9371. Both also have aromatic benzene rings and this correlation in structure brought about a fully miscible blend.

TCD-PC and N-PC was another fully miscible blend. This blend exhibited a single T_g at 249.37°C and is 1.46°C lower than the calculated Fox T_g of 250.83°C. Structurally, these two polymers are very similar with the aromatic benzene rings and the two large aliphatic ring systems. TCD-PC has the tricyclodecane group and the N-PC has a norbornene group, both of which are largely aliphatic. Their close structural similarities resulted in a fully miscible blend.

The final fully miscible blend was Lexan 145 BPA-PC and N-PC. This blend had a single T_g of 186.59°C and is less than 4°C away from the Fox T_g of 190.44°C. Like the other fully miscible blends, these two polymers had both aromatic and aliphatic character that was similar enough to bring about a fully miscible blend. The DSC for this blend is shown in Figure 10. The DSC scans for the other fully miscible blends can be found in the Appendix in Figures 26-29.

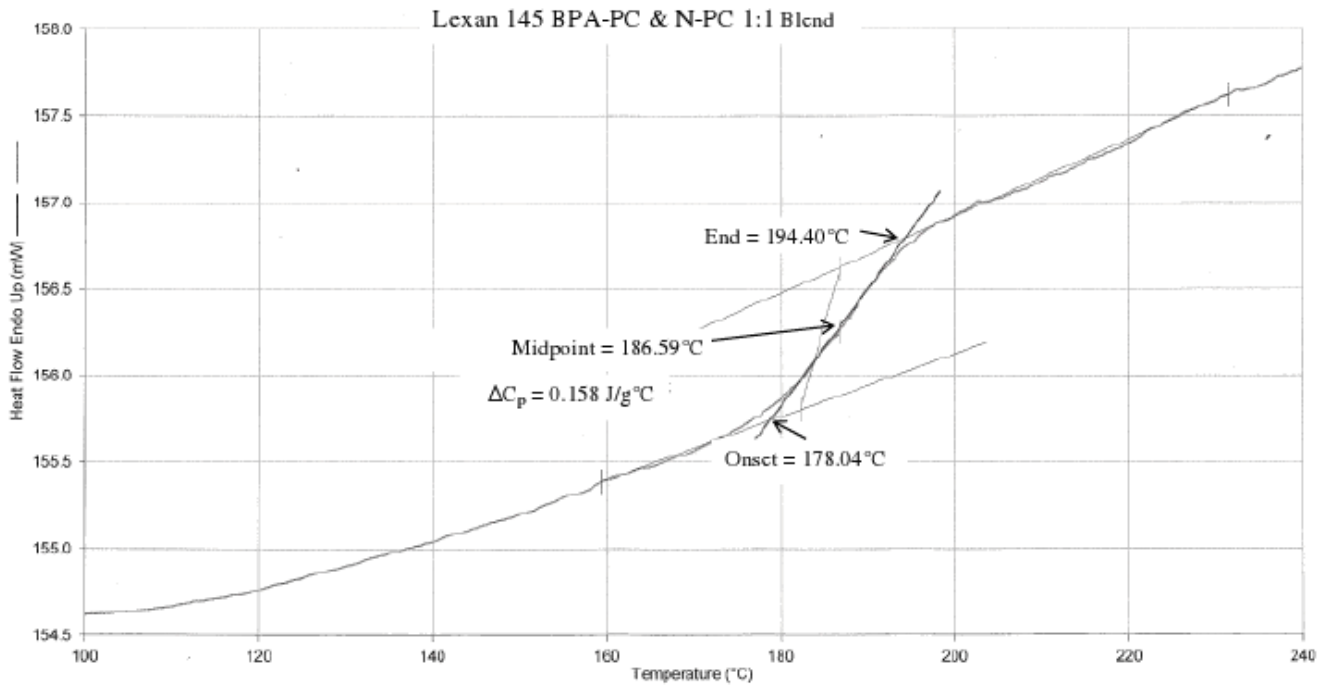


Figure 10. DSC scan of 50:50 Lexan 145 BPA-PC: N-PC Blend

3.7 Non-fully miscible PC-PC blends

Despite the full miscibility that was discovered between the above PC-PC blends, not all PC-PC blends were fully miscible. The blend of Teijin-PC and TCD-PC was partially miscible and had two T_g's in between the comprising polymers. The lower glass transition was 190.69°C and the higher was 233.99°C, with a Fox T_g of 201.17°C. The structures of these two polymers differed in that the structure of the TCD-PC is more more aliphatic in comparison with the BPA structure of the Teijin-PC. The saturated tricyclodecylidene group of TCD-PC is significantly more aliphatic that the isopropylidene group of the Teijin-PC, which was enough of a difference to make this a partially miscible blend. Since TCD-PC was not miscible with Teijin-PC, it would not be miscible with the higher molecular Lexan 145 BPA-PC.

There were two PC-PC blends that were immiscible or very slightly miscible, and both blends involved the 4MC-PC polymer. This was the only polycarbonate that that was completely aliphatic, as opposed to the other polycarbonates that had a mix of aliphatic and aromatic character. The blend of 4MC-PC and Teijin-PC exhibited a single T_g at 149.73°C, and the Fox T_g was 142.25°C. Individually, the glass transitions of 4MC-PC and Teijin-PC are 135.18°C and 149.48°C, respectively. The measured T_g just about matches the T_g for Teijin-PC, which indicated that they are immiscible. Also, the low ΔC_p for the blend 0.099 J/g°C indicated that there is another phase present that is unresolved by the DSC. This result also indicated that there would not be miscibility in a blend of 4MC-PC and Lexan 145 BPA-PC, since Lexan 145 BPA-PC is of a higher molecular weight than Teijin-PC.

The blend between BPA-TMC-PC 9371 and 4MC-PC was only very slightly miscible. There were two glass transitions, the lower at 123.14°C and the higher at

209.28°C. The individual T_g's of 4MC-PC and BPA-TMC-PC 9371 are 135.18°C and 213.39°C, respectively. The lower T_g of the blend is lower than the lowest T_g of the individual polymers; this phenomenon is discussed later. Since the higher T_g phase had a T_g that was only 4°C lower than that of the BPA-TMC-PC 9371, this blend is very slightly miscible. This is not surprising due to the differences in structure content between the two polymers.

These results showing the 4MC-PC has a very low miscibility with other polymers with a mix of aliphatic and aromatic character are consistent with the results of Cruz, et al. for methyl-substituted aliphatic polyester blends with BPA-PC, which were much less miscible than analogous linear aliphatic blends.[26]

There was another interesting result that came from the 4MC-PC and BPA-TMC-PC 9371 blend. There were two peaks that represented crystallization and melting temperatures that were present at 179.62°C and 258.98°C, respectively. Although each of the individual polymers are not crystalline, when blended together, a crystalline blend resulted. The crystallization and melting peaks are from the 4MC-PC phase because for there to be crystallization the polymer must be above its T_g. A similar phenomenon was seen in work by Cruz, Paul, et al., in BPA-PC/aliphatic polyester blends.[24] Although BPA-PC is not itself melt crystallizable under DSC conditions, its blends with aliphatic polyester were. The DSC for the 4MC-PC and BPA-TMC-PC 9371 blend is shown in Figure 11 and the DSC scans of the other two blends can be found in Figures 30 and 31 in the appendix.

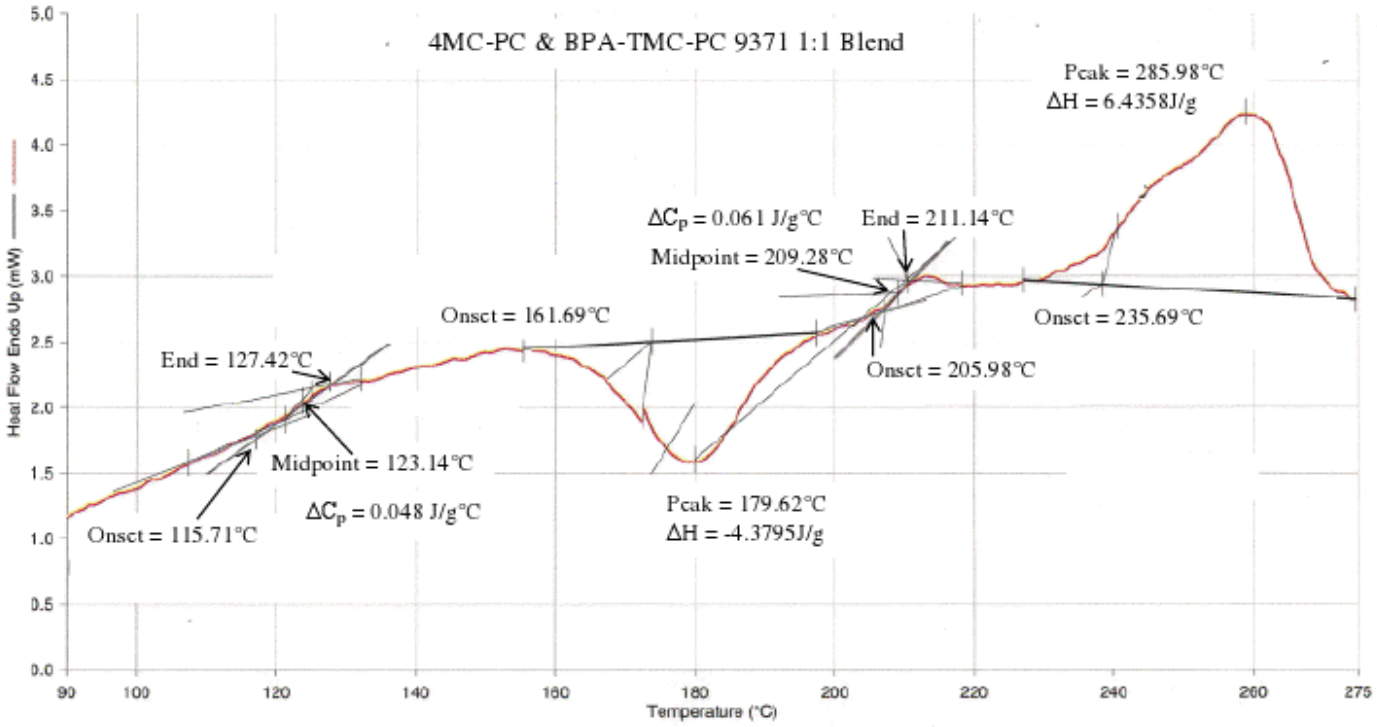


Figure 11. DSC scan of 50:50 4MC-PC:BPA-TMC-PC 9371 Blend

3.8 PE-PC miscibility results

None of the PC-PE and PE-PE blends studied were fully miscible. They all resulted in, at most, partial miscibility. The actual weight fractions of each polymer present in each phase of the blends were calculated and are shown in Table 7, and this reflects the miscibility of these non-fully miscible blends. In order to calculate the exact weight fractions in the polymer blends the Fox equation was used again from Equation 3.

Table 7. Weight Fraction in Polymer Blends

Polymer 1	Polymer 2	w_1	w_2
T(80)Az-N	BPA-TMC-PC 9371	0.28	0.72
T(80)Az-N (PE rich phase)	Lexan 145 (PE rich phase)	0.9983	0.0017
T(80)Az-N (PC rich phase)	Lexan 145 (PC rich phase)	0.21	0.79
T(80)Az-N (PE rich phase)	N-PC (PE rich phase)	0.83	0.17
T(80)Az-N (PC rich phase)	N-PC (PC rich phase)	0.28	0.72
T(80)Az-N (PC rich phase)	TCD-PC (PC rich phase)	0.33	0.67
T(80)Az-N (PC rich phase)	TCD-PC (PC rich phase)	0.13	0.87
T(80)Az-N (PC rich phase)	Teijin-PC (PC rich phase)	0.20	0.80
T(80)Az-N (PC rich phase)	Teijin-PC (PC rich phase)	____*	____*
T(60)Az-N (PE rich phase)	BPA-TMC-PC 9371 (PE rich phase)	____*	____*
T(60)Az-N (PC rich phase)	BPA-TMC-PC 9371 (PC rich phase)	0.42	0.58
T(60)Az-N (PE rich phase)	Lexan 145 (PE rich phase)	____*	____*
T(60)Az-N (PC rich phase)	Lexan 145 (PC rich phase)	____*	____*
T(60)Az-N	TCD-PC	0.54	0.46
T(60)Az-N	N-PC	0.22	0.78
T(60)Az-N	T(80)Az-N	0.84	0.16

*Composition could not be calculated from data (see discussion).

3.9 T(80)Az-N and PC blend results

From the calculated weight fractions, it can be determined which blends had the greater degree of miscibility from the non-fully miscible blends. The polycarbonates that

T(80)Az-N was blended with were BPA-TMC-PC 9371, Lexan 145 BPA-PC, Teijin-PC, N-PC, and TCD-PC. All of these blends were partially miscible with either two glass transitions or one T_g that was not close to the calculated Fox T_g. T(60)Az-N was blended with same polycarbonates, except Teijin-PC. Both T(60)Az-N and T(80)Az-N are copolyesters with both aromatic and aliphatic moieties, much like the polycarbonates they were blended with. However, it comparison to the polycarbonates, the two polyesters have more aliphatic character due to the norbornene ring in the N portion and the saturated seven carbon chain of the Az portion Due to the greater amount of aliphatic character in the polyesters than in the polycarbonates, the blends were no more than partially miscible.

Although all blends were partially miscible with T(80)Az-N, some polycarbonates were more miscible than others with T(80)Az-N. T(80)Az-N was more miscible with BPA-TMC-PC 9371, N-PC, and TCD-PC because they have more aliphatic character than Lexan 145 BPA-PC and Teijin-PC. The blend of T(80)Az-N and BPA-TMC-PC 9371 had a single T_g at 163.81°C, compared to the Fox T_g of 132.62°C. By looking at the weight fractions, it can be seen that the blend phase having a T_g of 163.81°C was PC rich with 28% of the blend being T(80)Az-N. There were two T_g's from the T(80)Az-N and N-PC blend at 94.34°C and 177.67°C, with a Fox T_g of 140.10°C. The lower T_g phase is PE rich with 17% being composed of N-PC, while the higher T_g phase is PC rich with 28% being composed of the PE. The blend of T(80)Az-N and TCD-PC had two T_g's at 184.38°C and 230.21°C, with a Fox T_g of 150.17°C. Both phases were rich in PC with the lower having 33% PE and the higher having 13% PE.

The blends of T(80)Az-N with Lexan 145 BPA-PC and Teijin-PC were less partially miscible. The blend with Lexan 145 BPA-PC resulted in two T_g's at 74.95°C and 133.25°C,

with a Fox T_g of 109.86°C. The lower T_g phase is PE rich with 99.8% T(80)Az-N and the higher is PC rich with 79% Lexan 145 BPA-PC. The blend of T(80)Az-N and Teijin-PC had two T_g's at 132.47°C and 157.74°C, compared to the Fox T_g of 108.59°C. The lower T_g was PC rich with 80% Teijin-PC. However, a weight fraction for the higher T_g phase could not be calculated because it was higher than the highest T_g of the individual polymers. This phenomenon is explained later.

BPA-TMC-PC 9371, N-PC, and TCD-PC have more aliphatic character in their structural content than Lexan 145 BPA-PC and Teijin-PC do. T(80)Az-N has a large amount of aliphatic character, so even though the polycarbonates do not have as much, it makes sense for it to be more miscible with the polycarbonates with the most aliphatic character. The DSC for the T(80)Az-N and Teijin-PC blend is shown in Figure 12 and the other spectra can be found in the appendix in Figures 32-35.

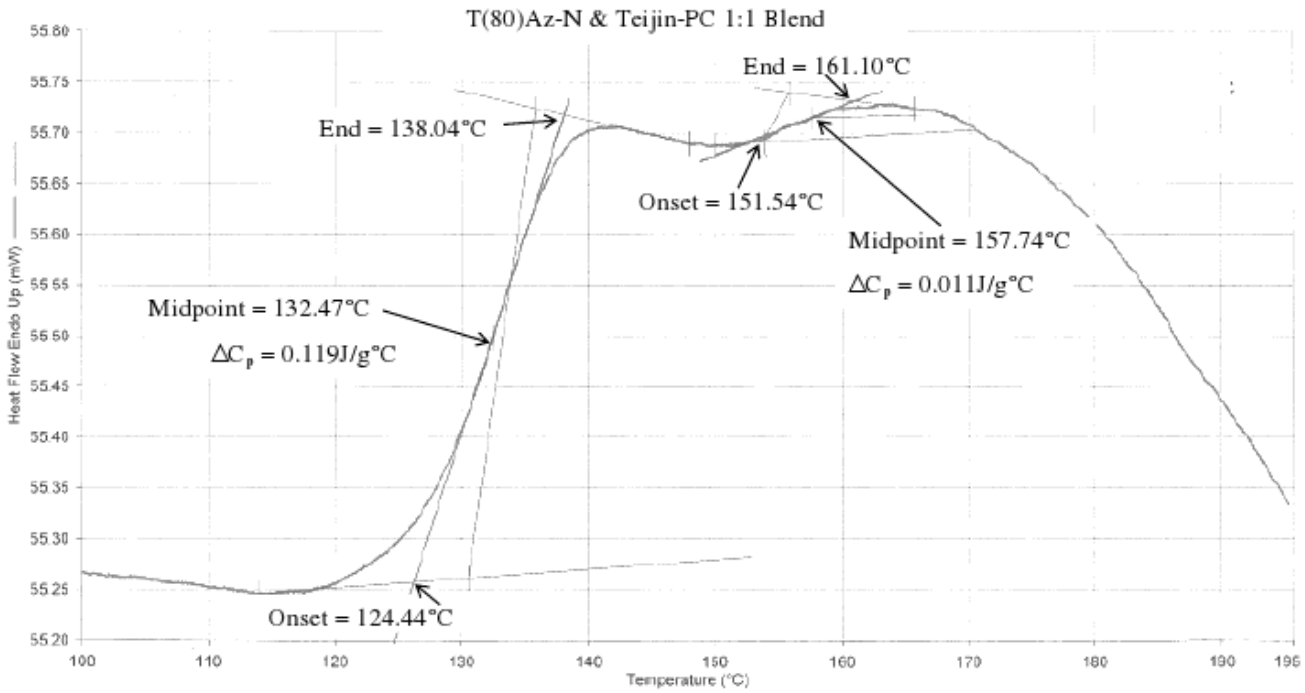


Figure 12. DSC scan of 50:50 T(80)Az-N:Teijin-PC Blend

3.10 T(60)Az-N and PC blend results

From the polycarbonates blended with T(60)Az-N, all but one was partially miscible. T(60)Az-N was partially miscible with TCD-PC, N-PC, and BPA-TMC-PC 9371, which all have aliphatic ring systems in their structural content. When it was blended with TCD-PC, one T_g resulted at 195.00°C with a Fox T_g of 199.65°C. Although the measured T_g is proximately close to the Fox T_g, the DSC trace was incredibly noisy with a variety of other peaks present. This blend was slightly PE rich, with 54% T(60)Az-N. The blend of T(60)Az-N and N-PC had a single T_g of 212.53°C compared to the Fox T_g of 187.14°C. This blend was PC rich with 78% N-PC. When T(60)Az-N was blended with BPA-TMC-PC 9371 two T_g's resulted at 141.48°C and 182.99°C and had a Fox T_g of 177.86°C. The lower T_g was lower than that of the polymer with the lowest T_g and, therefore, the weight fractions could not be calculated. The higher T_g phase was slightly PC rich with 58% BPA-TMC-PC 9371. These polycarbonates have more aliphatic character than Lexan 145 BPA-PC, which when blended with T(60)Az-N was immiscible. The DSC for the T(60)Az-N and N-PC blend is very broad and is shown in Figure 13 and the remaining PC-PE DSC traces can be found in the appendix in Figures 36 and 37. This broad peak, 50 degrees separating the onset from the endpoint, indicates that although it's a single phase, there is a degree of heterogeneity in the blend.

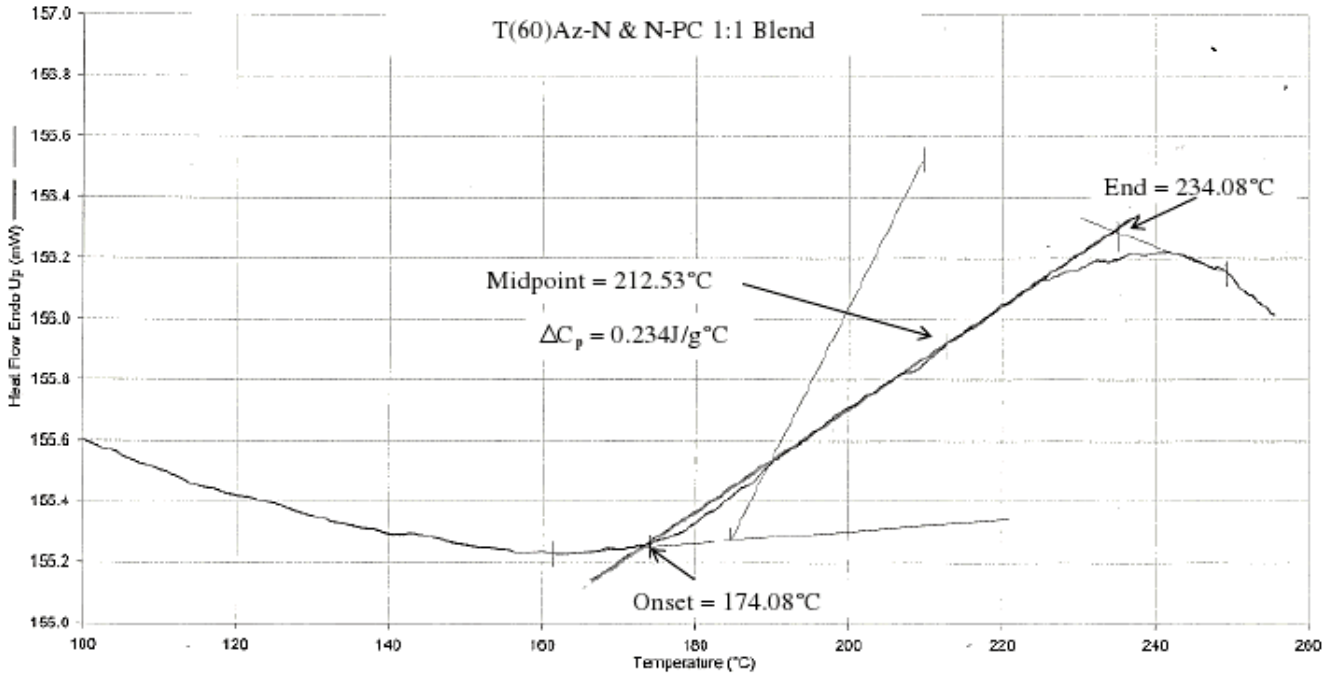


Figure 13. DSC scan of 50:50 T60)Az-N:N-PC Blend

The blend of T(60)Az-N with Lexan 145 BPA-PC had two T_g's that exhibited a PE rich phase and a PC rich phase, which were entirely composed of the polyester and the polycarbonate, respectively. This blend had two T_g's at 143.49°C and 153.94°C, with a Fox T_g of 149.92°C. Neither of these fall between the T_g's of the individual polymers with the T_g's of T(60)Az-N and Lexan145 BPA-PC, 147.17°C and 152.71°C respectively. The lower T_g of the blend was lower than the T_g of the polyester and the higher T_g of the blend was higher than the T_g of the polycarbonate. This seemingly paradoxical result can be explained by the lower molecular weight portion of the Lexan 145 BPA-PC, which can be composed of very low molecular weight oligomers having low T_g's, dissolving in the PE phase, lowering its T_g and leaving behind a higher T_g PC phase. This makes it impossible to calculate the composition of the two phases from their constituent T_g's. The presence of low molecular weight fractions is also responsible for other T_g results lying outside the constituent T_g range of the blends. This DSC scan can be found in Figure 38 in the appendix.

The results of the T(60)Az-N and T(80)Az-N blends with with BPA-PC is understandable when relating them to the work of Yang and Yetter.[21] Yang and Yetter studied T(40)Az-N, which has more aromatic content than aliphatic, with Lexan 145 BPA-PC. T(40)Az-N was miscible with Lexan 145 BPA-PC, while the results in this study showed that Lexan 145 BPA-PC was partially miscible with T(80)Az-N and immiscible with T(60)Az-N. Since Lexan 145 BPA-PC has more aromatic content than aliphatic, it should more miscible with T(40)Az-N, which also has more aromatic character than aliphatic. Since T(60)Az-N and T(80)Az-N have more aliphatic content, they are not as miscible with Lexan 145 BPA-PC.

The two polyesters, T(60)Az-N and T(80)Az-N, were blended together and resulted with a single T_g at 133.49°C compared to its Fox T_g of 107.60°C. Since the measured T_g was not close to the calculated Fox T_g, this blend was determined to be partially miscible. The T(60)Az-N took better to the blend as it was 84% T(60)Az-N and 16% T(80)Az-N. These copolyesters have the same structure; however their overall composition is not the same. The ratio of T:Az for T(60)Az-N and T(80)Az-N is 0.4:0.6 and 0.2:0.8, respectively. T represents an aromatic component, while Az represents the aliphatic component. This difference between their content, although not very large, was enough to alter their solubility and to prevent the formation of a fully miscible blend. This phenomenon has been observed in other copolymer blends of differing compositions where there was low miscibility and phase separation.[31] The calculated weight fractions of the T(60)Az-N and T(80)Az-N blend showed that there was a greater fraction of T(60)Az-N miscible in the blend and their differences in ratios of aliphatic and aromatic group content explains the partial miscibility. The DSC spectrum for this blend is shown in Figure 14.

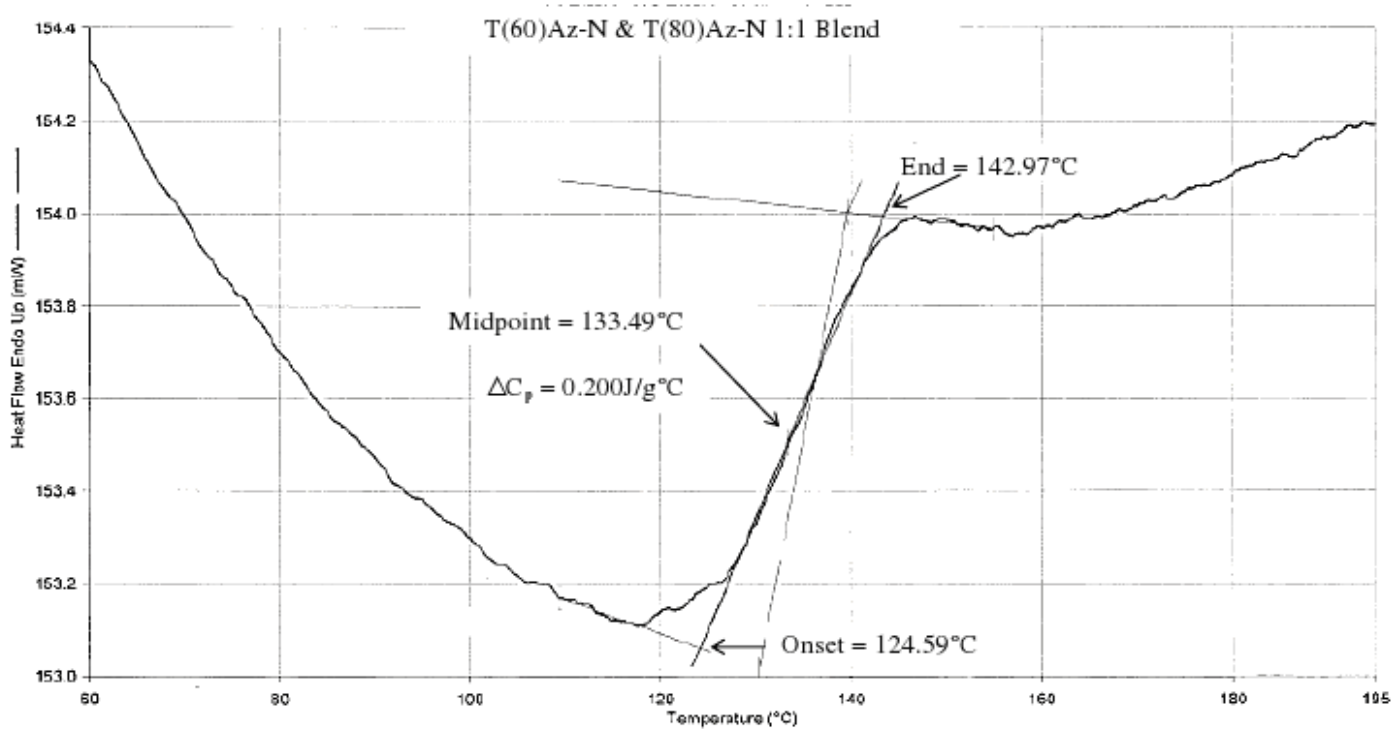


Figure 14. DSC scan of 50:50 T(60)Az-N:T(80)Az-N Blend

3.11 Polymer blend series

Based on the results of the 50:50 blends, three blends were chosen to expand into a series in which various blend compositions were studied. The expanded compositions studied were 0:100, 25:75, 50:50, 75:25, and 100:0. The two miscible blends expanded into a series were BPA-TMC-PC 9371 and Lexan 145 BPA-PC, and N-PC and Lexan 145 BPA-PC. The Teijin-PC and TCD-PC blend was partially miscible and was also expanded into a series. All DSC scans for these series can be found in the Appendix in Figures 39-44.

The Lexan 145 BPA-PC and BPA-TMC-PC 9371 blend showed be very miscible based on the results of the 50:50 blend as it had a single T_g in very close proximity to the Fox T_g. The data from the entire series of compositions is shown in Table 8. The Fox T_g and Couchman T_g were calculated for each composition and the measured T_g for all compositions was no more than 2°C off from the Fox and Couchman T_g's. This further confirms the full

miscibility of this blend and these results are plotted in Figure 15. The onset, midpoint, and endpoint for all compositions were plotted in comparison to the Fox and Couchman equation lines. As it can be seen, the data forms a relatively straight line with a slight concave upward curve. The Fox equation line and Couchman equation line fall in the middle of the three points each representing the onset, midpoint, and endpoint for all compositions and both almost fall on the midpoint through the entire plot. This is an example of a well behaved miscible blend.

Table 8. Series DSC Data for BPA-TMC-PC 9371:Lexan 145 BPA-PC Blend

BPA-PC-TMC 9371:Lexan 145	Onset (°C)	Mid (°C)	End (°C)	ΔCp (J/g°C)	Fox (°C)	Couchman (°C)
0:100	148.89	152.71	154.9	0.19	-----	-----
25:75	161.83	165.16	168.92	0.25	166.42	165.33
50:50	175.68	181.36	186.33	0.20	181.03	179.45
75:25	189.34	195.95	200.54	0.25	196.65	195.35
100:0	208.15	213.39	216.56	0.16	-----	-----

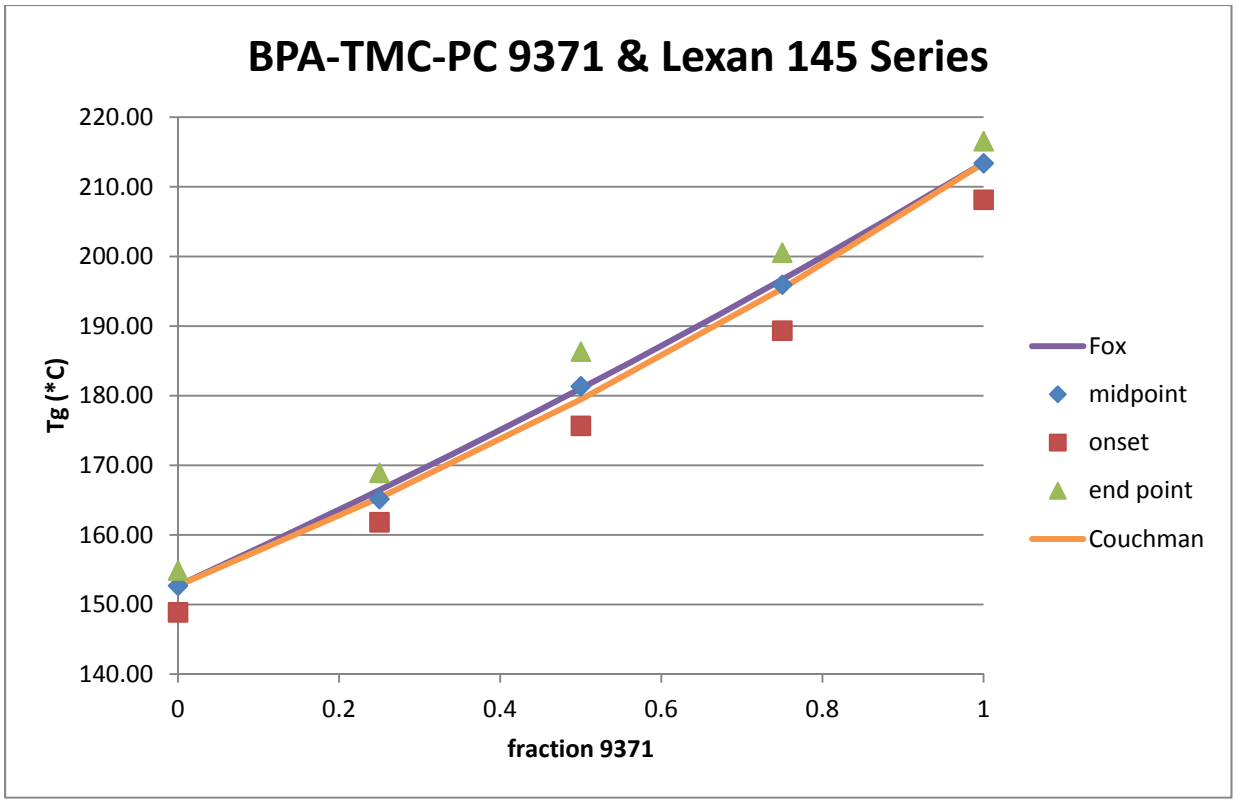


Figure 15. BPA-TMC-PC 9371:Lexan 145-BPA-PC Series Blend Data Plot

The N-PC and Lexan 145 BPA-PC blend was another fully miscible blend that exhibited a single T_g in close proximity to the calculated Fox and Couchman T_g's. The onset, midpoint, end point, ΔC_p, Fox T_g, and Couchman T_g are shown in Table 9. The Couchman equation gives a slightly better fit to the data than the Fox equation does. Each of the calculated T_g's were very close to the measured T_g's at the varying compositions being that they were no more than 6°C different, showing the blend's full miscibility. The data are also plotted in Figure 16. The measured T_g points form a slight concave curve and the Fox and Couchman equation lines follow this curve as they fall in between the three points for each composition and hold fairly close to the midpoint of the curve. The correlation between the measured T_g's at each composition to the calculated T_g's for each composition further shows that this is a fully miscible blend across all compositions.

Table 9. Series DSC Data for N-PC:Lexan 145 BPC-PC Blend

N-PC:Lexan 145 BPA-PC	Onset (°C)	Mid (°C)	End (°C)	ΔCp (J/g°C)	Fox (°C)	Couchman (°C)
0:100	148.89	152.71	154.90	0.19	-----	-----
25:75	162.88	168.92	176.20	0.15	170.77	169.62
50:50	178.04	186.59	194.40	0.16	190.44	188.74
75:25	200.00	206.44	217.35	0.13	211.92	210.51
100:0	223.12	235.50	241.83	0.16	-----	-----

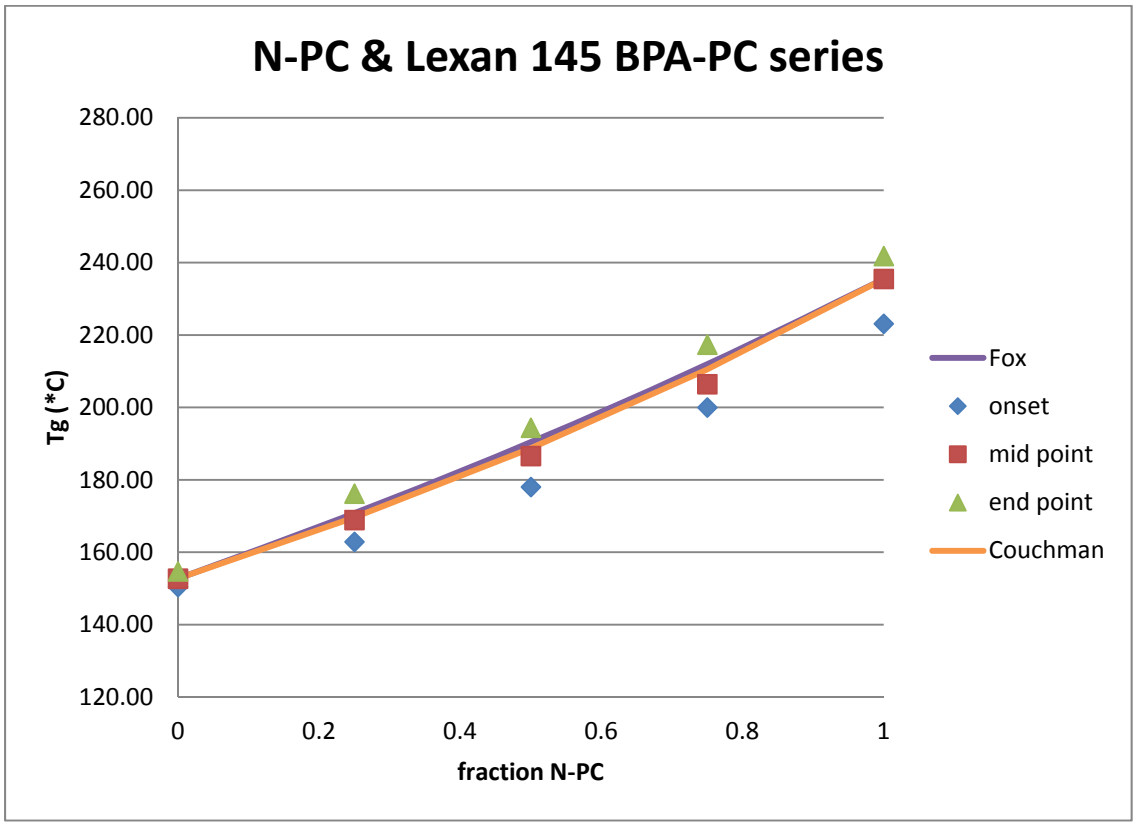


Figure 16. N-PC:Lexan 145 BPA-PC Series Blend Data Plot

The TCD-PC and Teijin-PC blend was partially miscible as it had two T_g's intermediate between the glass transitions of the constituent polymers. The data obtained from the series of compositions that were tested are shown in Table 10. Each composition exhibited two T_g's, with the Fox and Couchman T_g's falling in between. The data were plotted and are shown in Figure 17. The Fox and Couchman T_g lines are slightly concave

upward curves and fall between the data for the low and the high T_g, while the shape of the data points for the compositions of the blend is convex. Every data point for the high T_g's falls above the Fox T_g line, while every data point except one for the low T_g's falls below the line. For a partially miscible blend, the ideal behavior would be to have all T_g high points fall above the predicted line and all T_g low points fall below. The Couchman line falls perfectly between the high and low T_g's. This blend still proved to be a partially miscible blend. From these data, it can be seen that Teijin-PC is miscible with TCD-PC up to about 20-wt% Teijin-PC, and only partially miscible thereafter.

Table 10. Series DSC Data for Teijin-PC: TCD-PC Blend

Teijin-PC:TCD-PC	Onset (°C)	Mid (°C)	End (°C)	ΔCp (J/g°C)	Fox (°C)	Couchman (°C)
0:100	145.99	149.47	151.90	0.20	-----	-----
25:75 L	160.96	165.19	171.50	0.15	172.91	175.99
25:75 H	199.80	201.42	202.28	0.05		
50:50 L	183.08	190.69	198.82	0.18	200.42	204.36
50:50 H	225.72	233.99	240.74	0.08		
75:25 L	214.48	221.91	236.44	0.08	231.64	234.72
75:25 H	242.84	243.35	243.80	0.010		
100:0	261.92	267.11	270.48	0.20	-----	-----

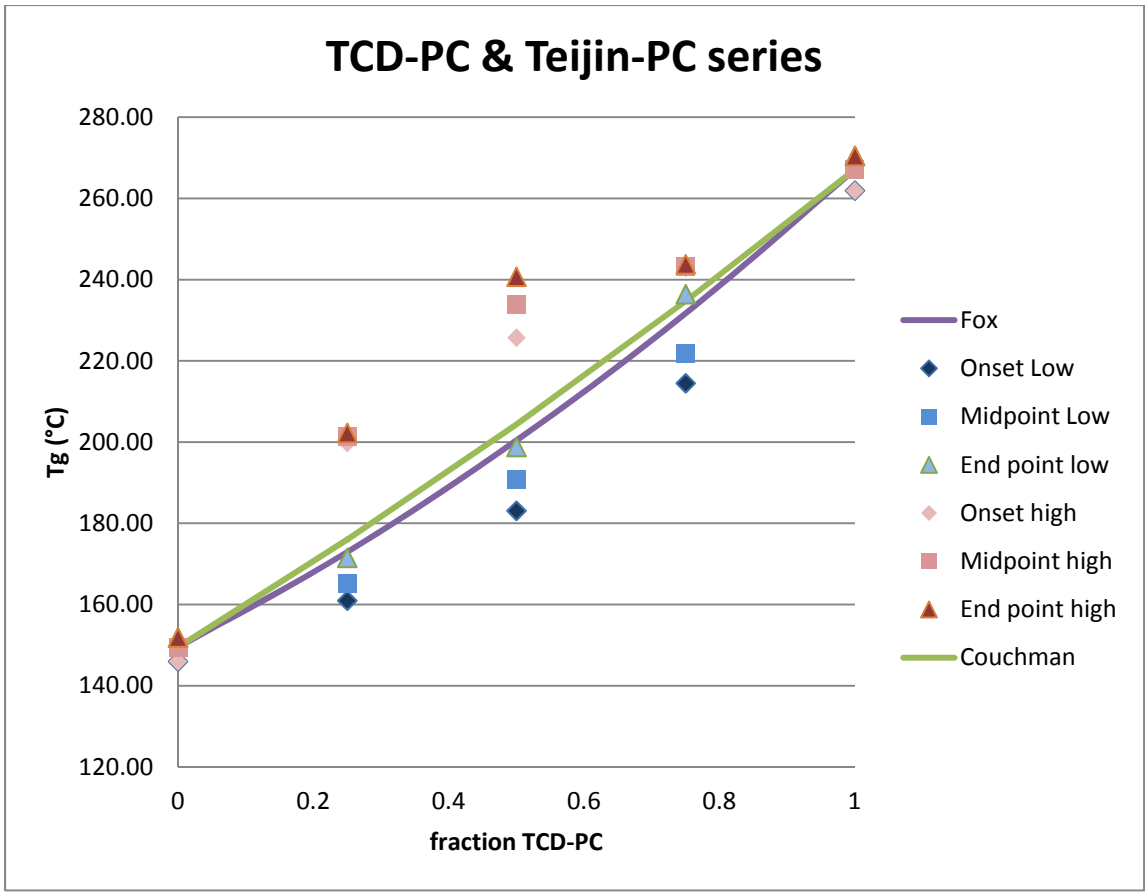


Figure 17. TCD-PC:Teijin-PC Series Blend Data Plot

4.0 Conclusions and Future Directions

The present research explored the miscibility of polymer blends involving polycarbonates and polyesters with differing structural content and it was proposed that blends with similar structural content will result in a miscible blend, and with increasing differences there may be less miscibility. The relationship between blend miscibility and constituent polymer structure was established by examining blends of polyesters and polycarbonates having a range of aliphatic and aromatic character. Solution blending and precipitation was used to prepare blends and differential scanning calorimetry proved to be a convenient and reliable method for characterizing the blend miscibility and phase behavior. It was found that blends with similar structural content resulted in a miscible blend, and with increasing differences there was less miscibility.

There were five fully miscible blends discovered, which were Lexan 145 BPA-PC and BPA-TMC-PC 9371, N-PC and BPA-TMC-PC 9371, TCD-PC and BPA-TMC-PC 9371, N-PC and Lexan 145 BPA-PC, and TCD-PC and N-PC. All these blends exhibited a single T_g in between the T_g's of the constituent polymers and close to the calculated Fox T_g. T(80)Az-N blends with BPA-TMC-PC 9371, Lexan 145 BPA-PC, Teijin-PC, N-PC, TCD-PC, and T(60)Az-N were partially miscible, along with BPA-TMC-PC 9371 and T(60)Az-N, Teijin-PC and TDC-PC, N-PC and T(60)Az-N, and TCD-PC and T(60)Az-N. The blend that showed to be immiscible was T(60)Az-N and Lexan 145. All partially miscible or immiscible blends exhibited a single T_g not close to the calculated T_g, or two T_g's more similar to the T_g's of the constituent polymers in the blend.

The polymer blends made in this study can be used for a variety of applications due to their properties. Blends of polycarbonates and polyesters are able to be used in the

automobile industry and are used to make various parts of a car, including the bumper. Also, the blends that were made that had higher thermal stability could be used in the medical industry as they are capable of being sterilized.

For future work that can be done on this topic, computational studies on additional blends should be done to determine more quantitatively the thermodynamic group interaction parameters of the blends. This would involve the synthesis and characterization of a greater range of molecular weights and wider BPA-TMC-PC polymer compositions. Also, there should be a follow up on the 4MC-PC and BPA-TMC-PC 9371 polymer blend because individually these polymers do not crystallize, but as a blend there showed to be crystallization and melting temperatures from the DSC results. More could be learned about these polymers individually and as a blend to see if there can be a better understanding of why they crystallize as a blend.

The temperature dependence, phase morphology, and composition dependence of miscibility could be looked at as well, in order to learn more about the properties and behavior of these blends. This could be done through scattering techniques or a microscope hot stage on which a blend film sample is placed and through which a laser beam is passed. If the blend is cloudy or not fully miscible, the laser beam will scatter, and if it is clear or miscible, the beam will shine through.

5.0 Appendix

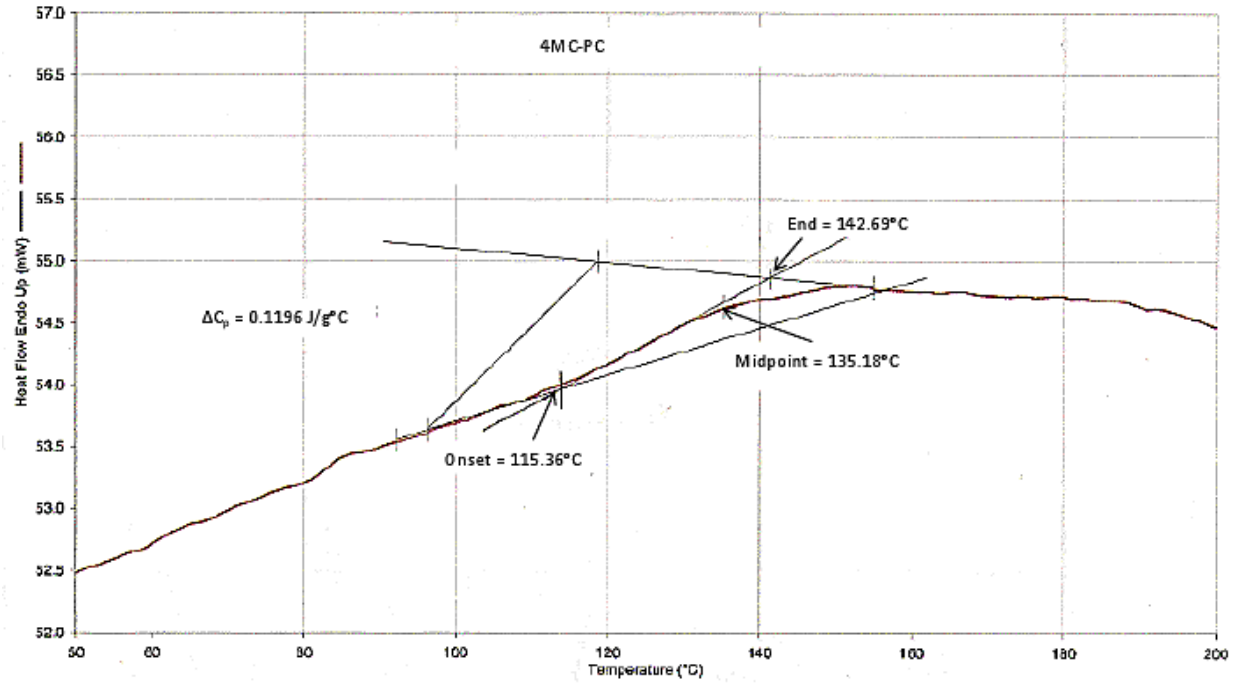


Figure 18. DSC Scan of 4MC-PC

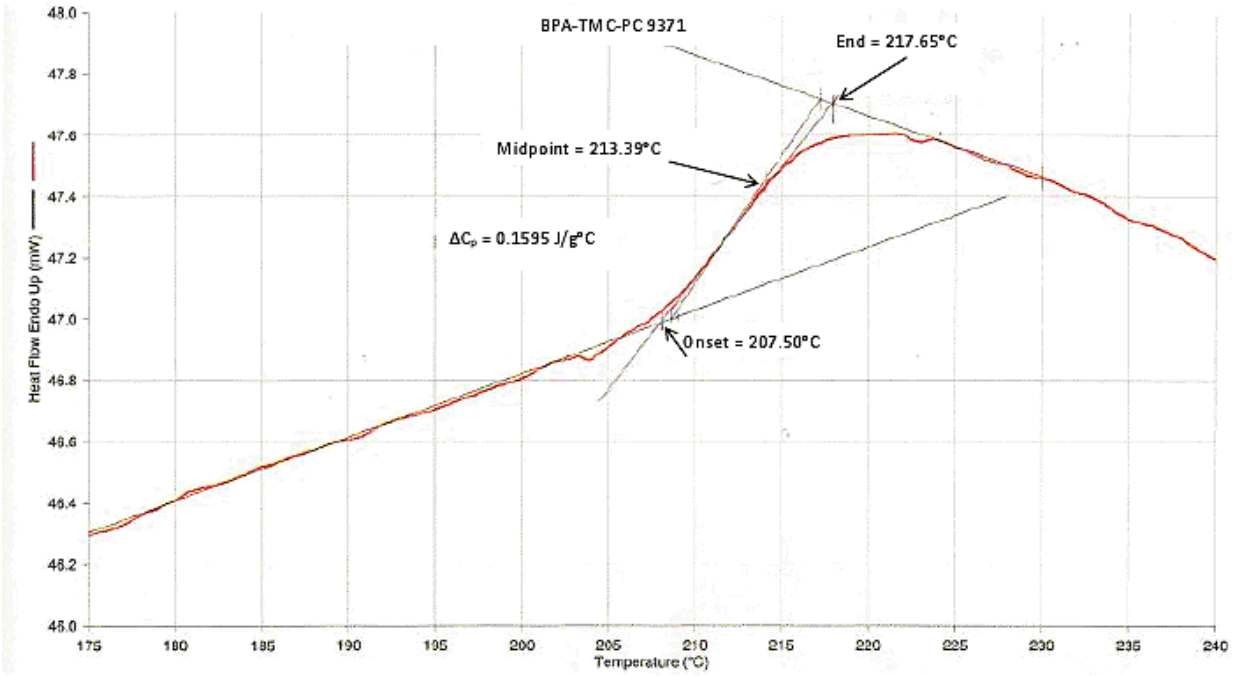


Figure 19. DSC Scan of BPA-TMC-PC 9371

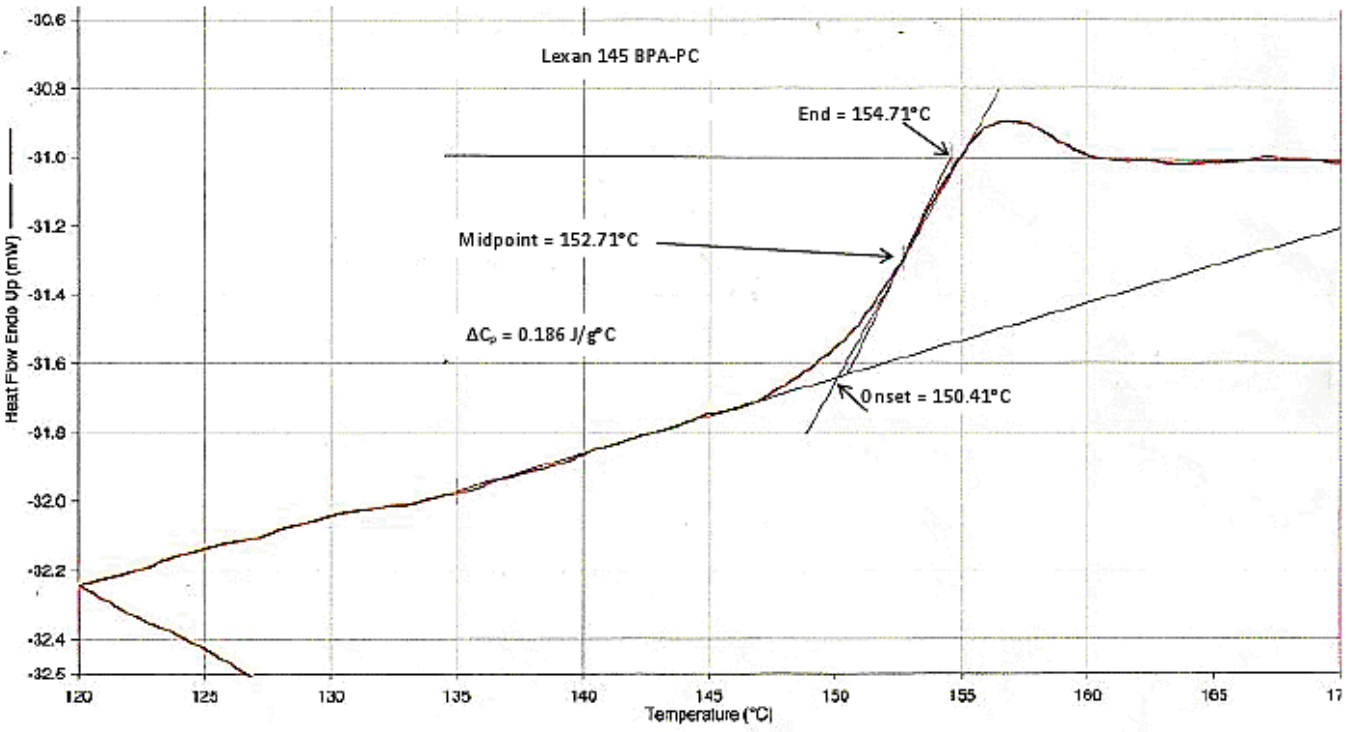


Figure 20. DSC Scan of Lexan 145 BPA-PC

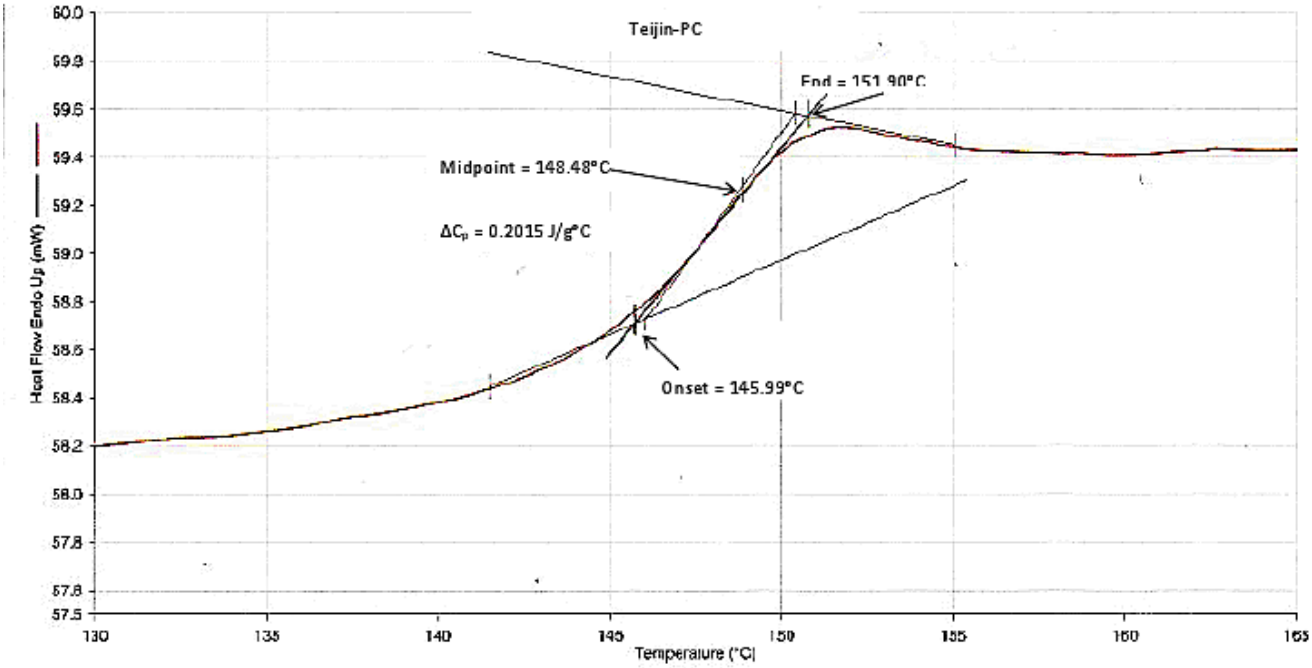


Figure 21. DSC Scan of Teijin-PC

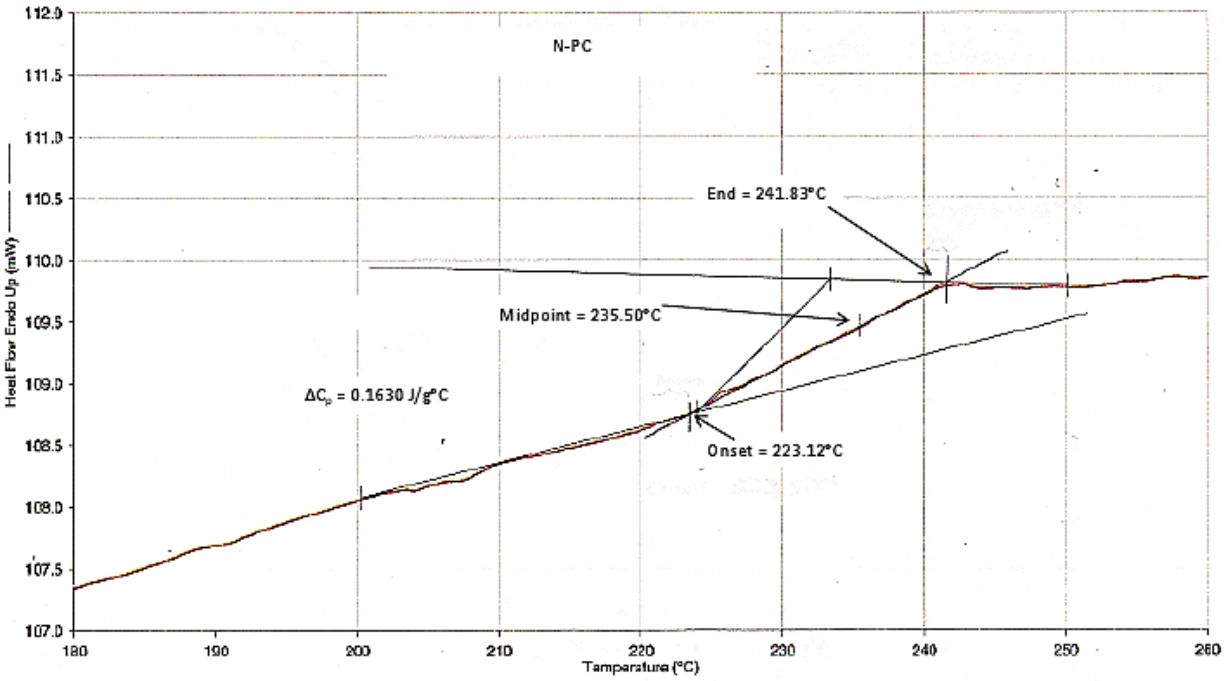


Figure 22. DSC Scan N-PC

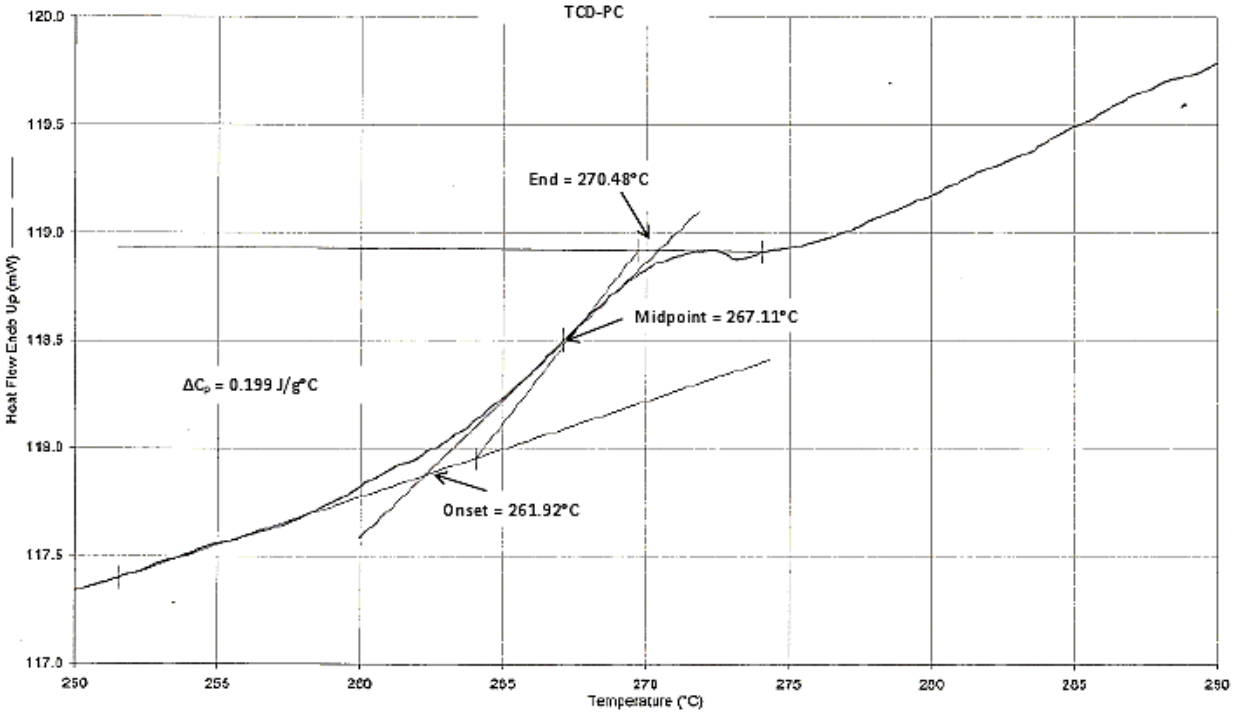


Figure 23. DSC Scan of TCD-PC

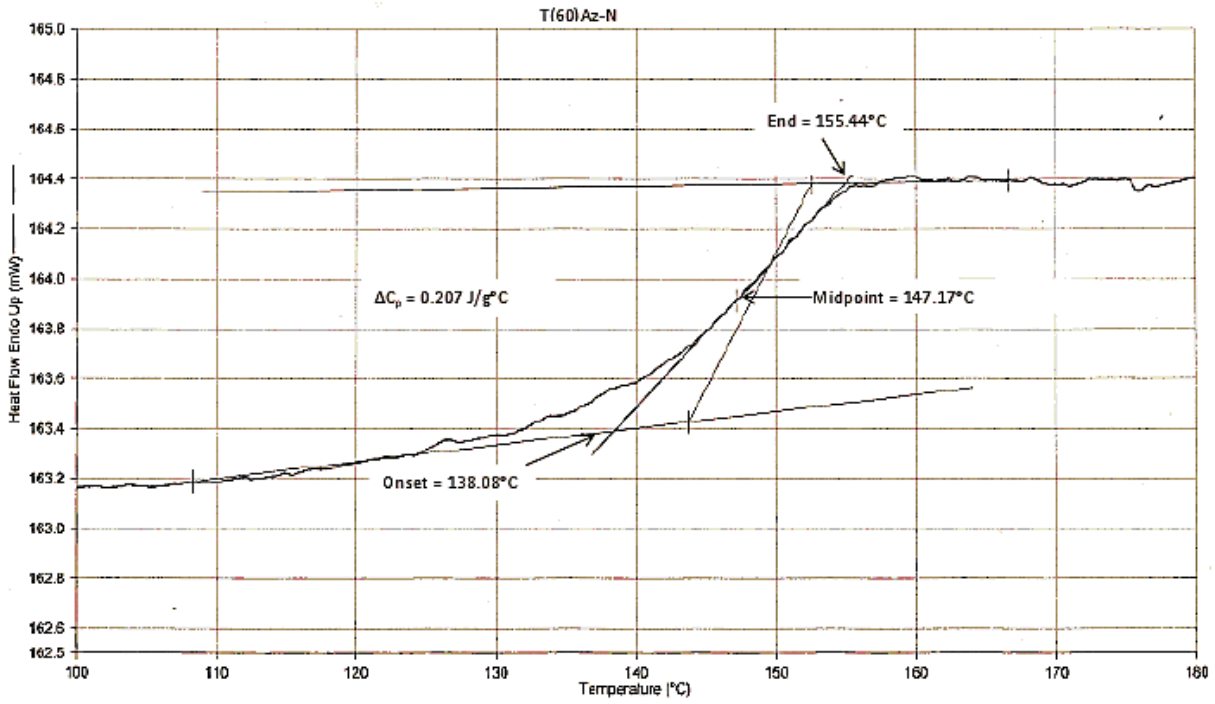


Figure 24. DSC Scan of T(60)Az-N

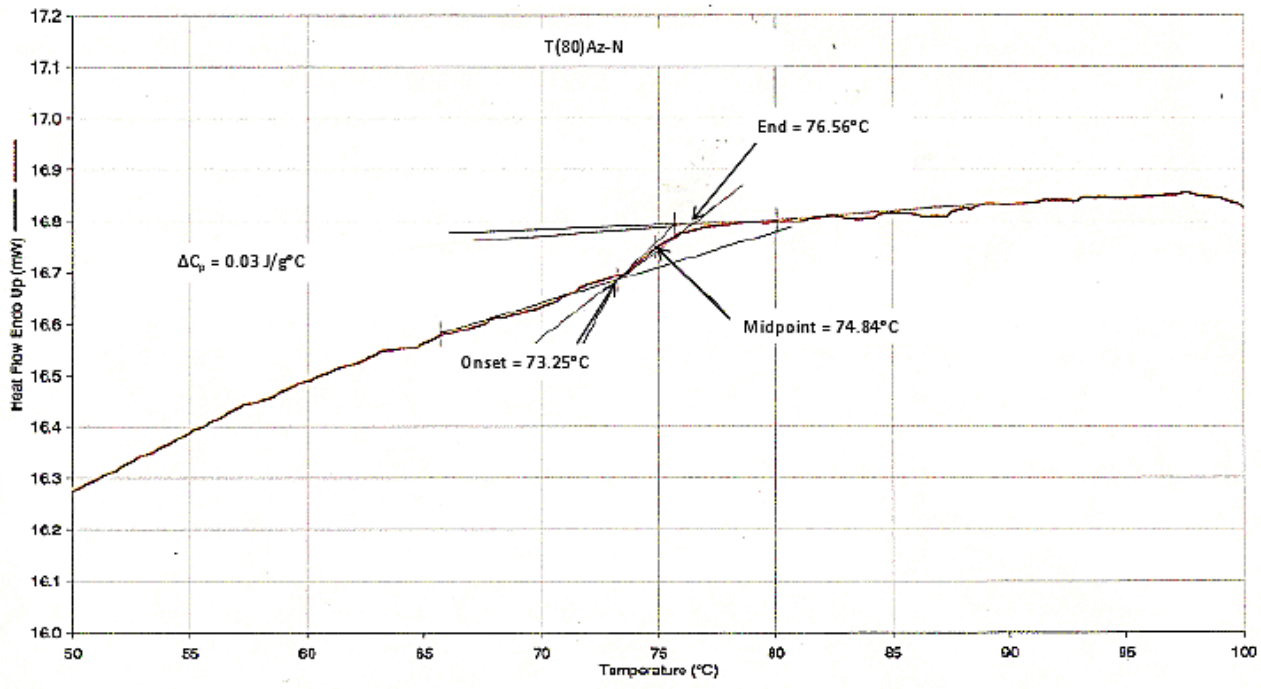


Figure 25. DSC Scan of T(80)Az-N

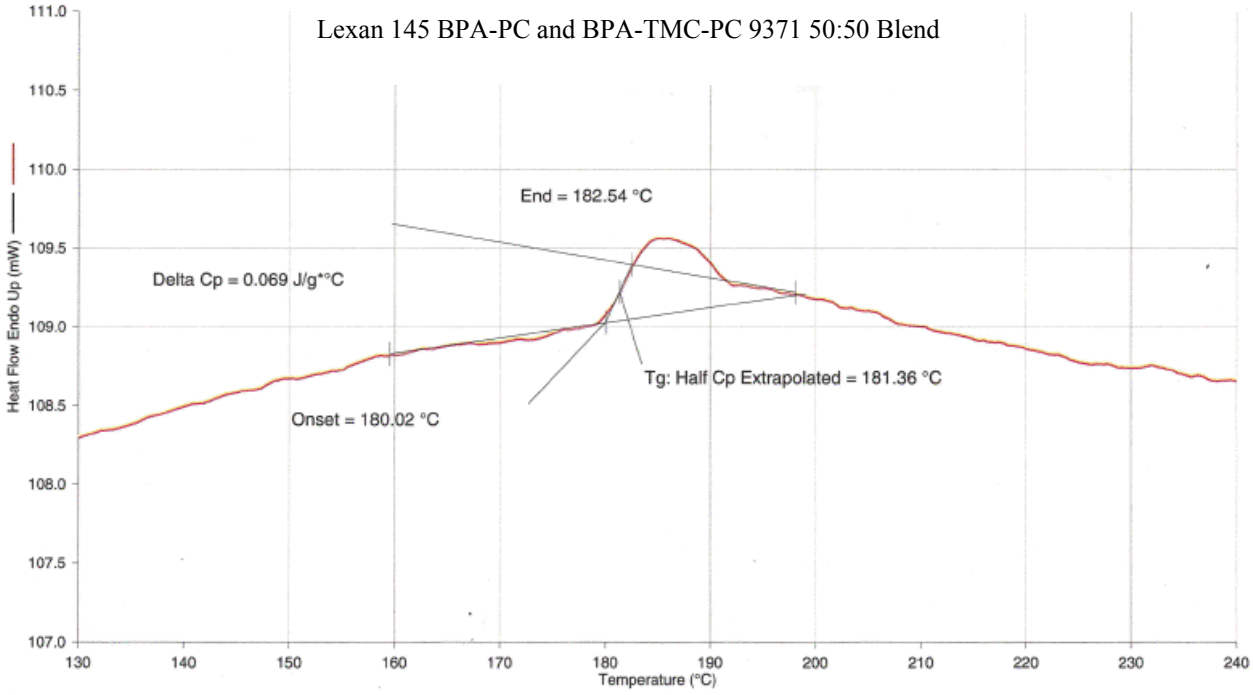


Figure 26. DSC Scan of Lexan 145 BPA-PC and BPA-TMC-PC 9371 50:50 Blend

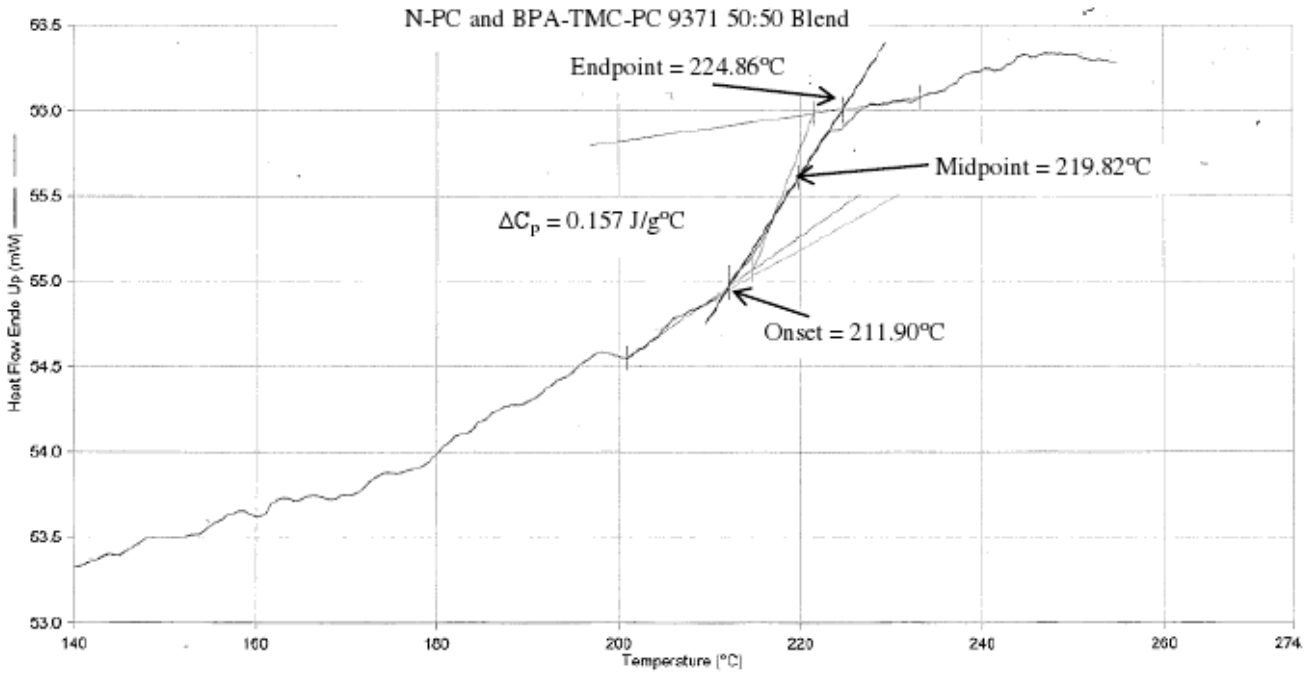


Figure 27. DSC Scan of N-PC and BPA-TMC-PC 9371 50:50 Blend

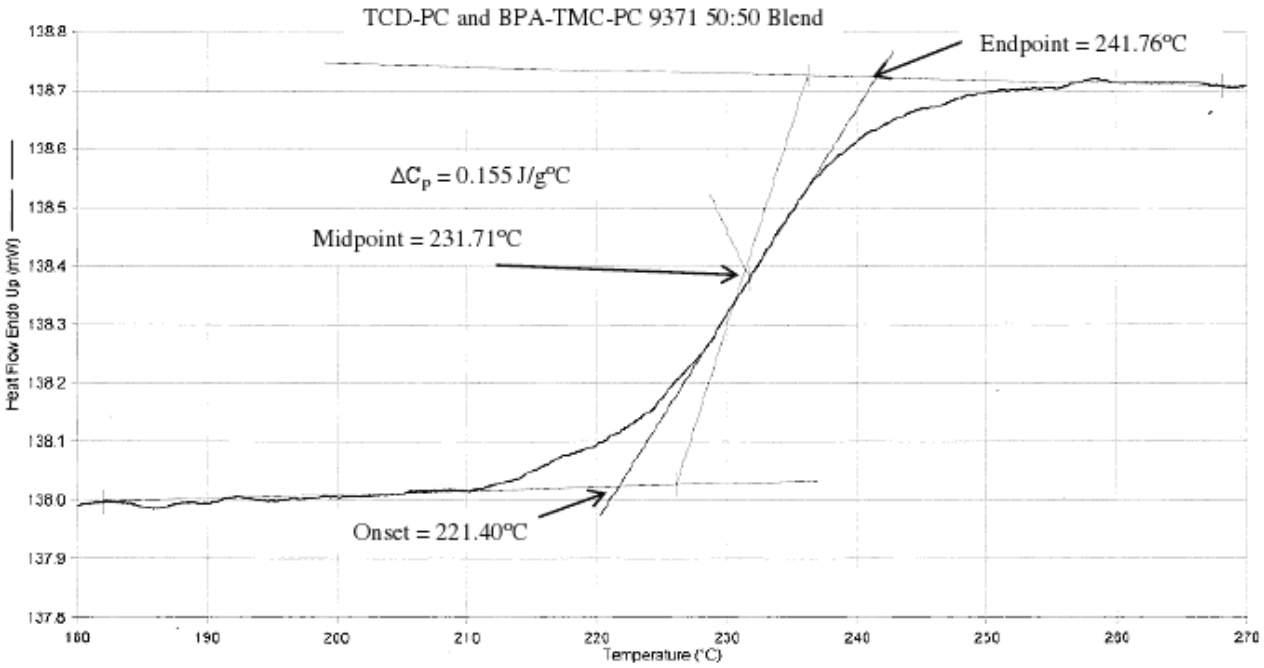


Figure 28. DSC Scan of TCD-PC and BPA-TMC-PC 9371 50:50 Blend

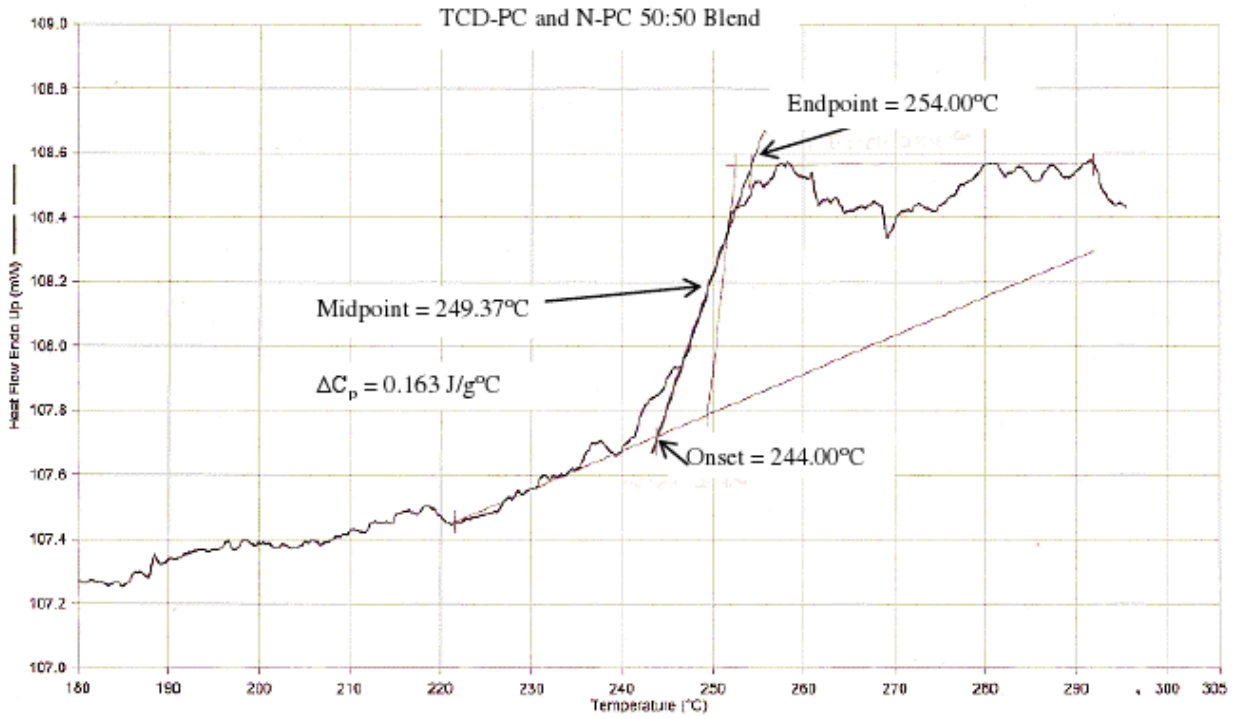


Figure 29. DSC Scan of TCD-PC and N-PC 50:50 Blend

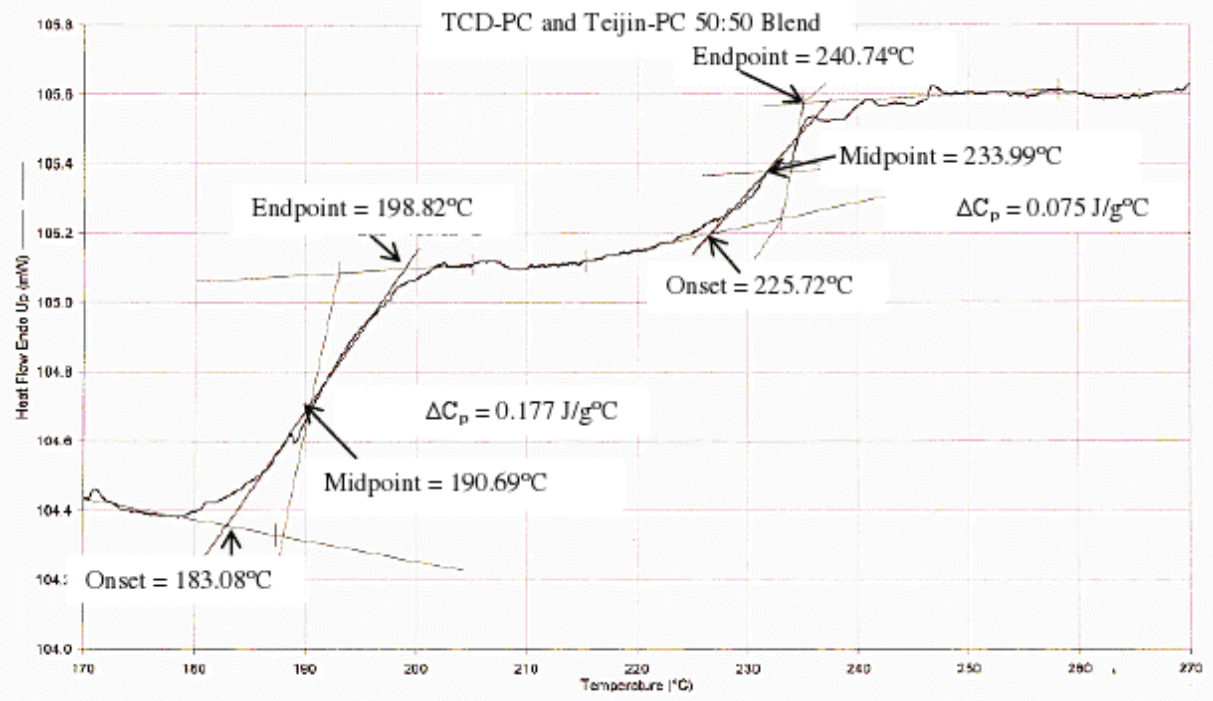


Figure 30. DSC Scan of TCD-PC and Teijin-PC 50:50 Blend

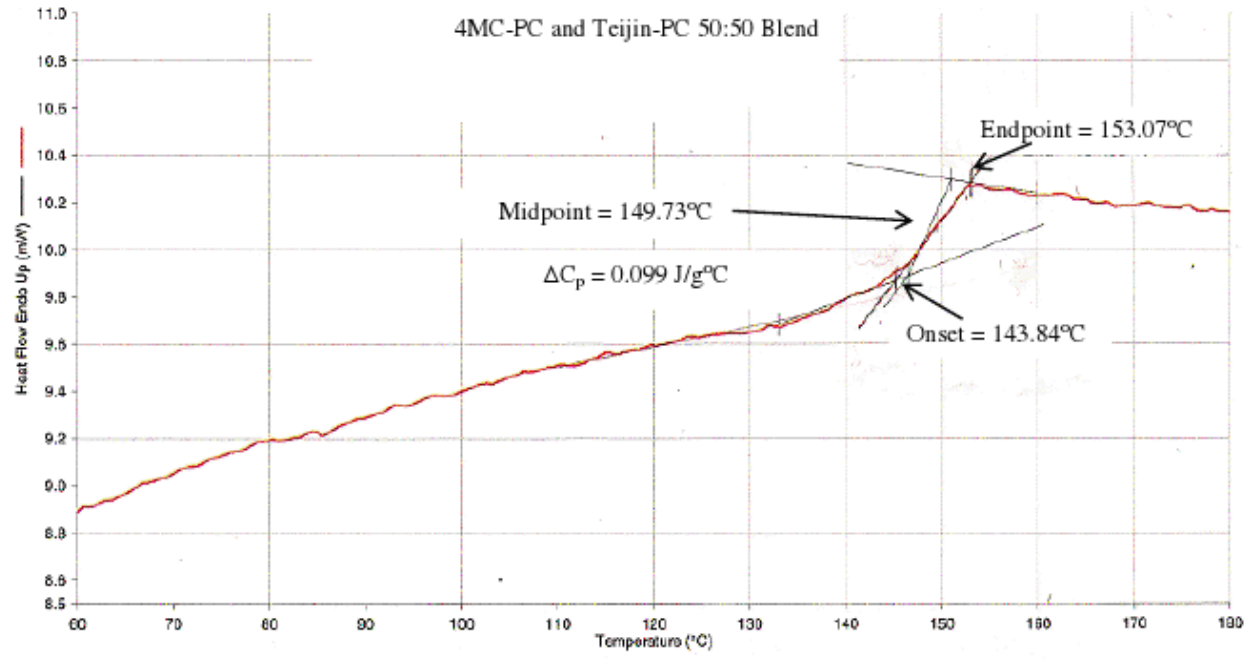


Figure 31. DSC Scan of 4MC-PC and Teijin-PC 50:50 Blend

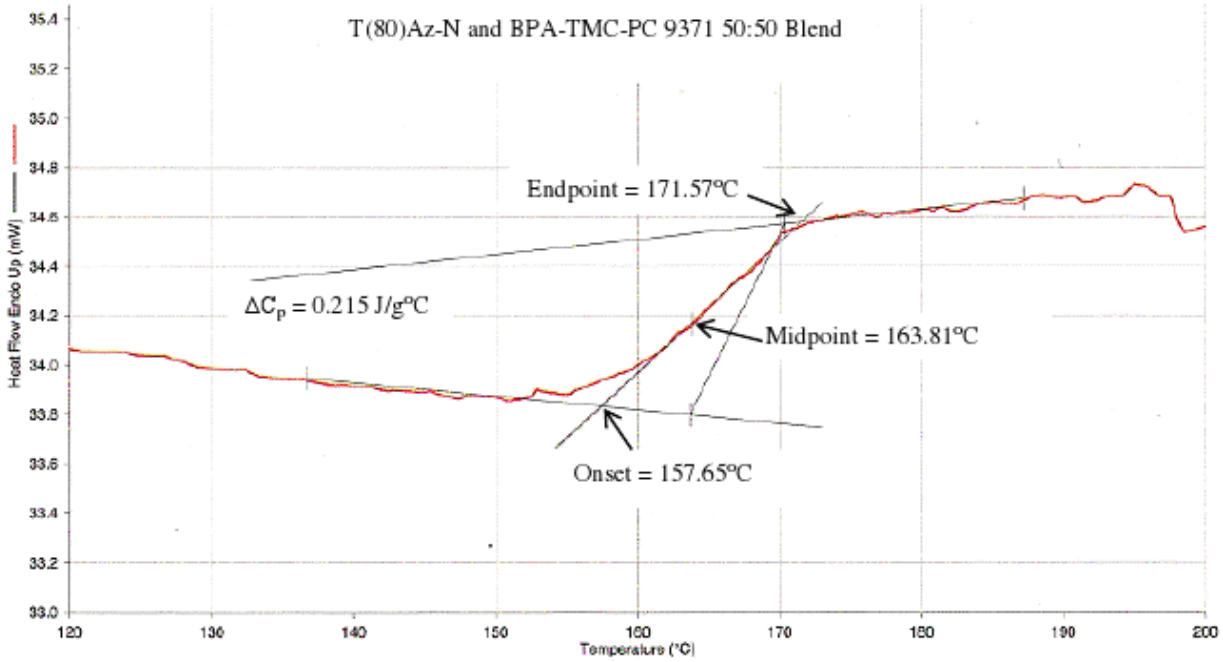


Figure 32. DSC Scan of T(80)Az-N and BPA-TMC-PC 9371 50:50 Blend

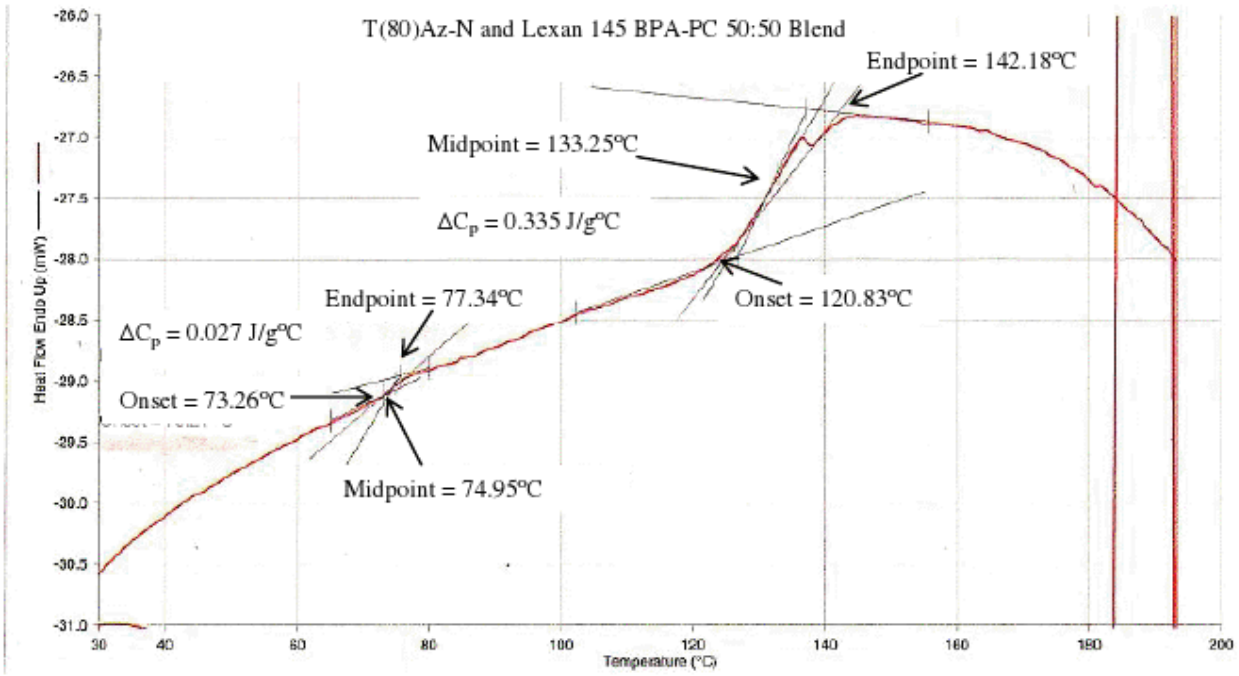


Figure 33. DSC Scan of T(80)Az-N and Lexan 145 BPA-PC 50:50 Blend

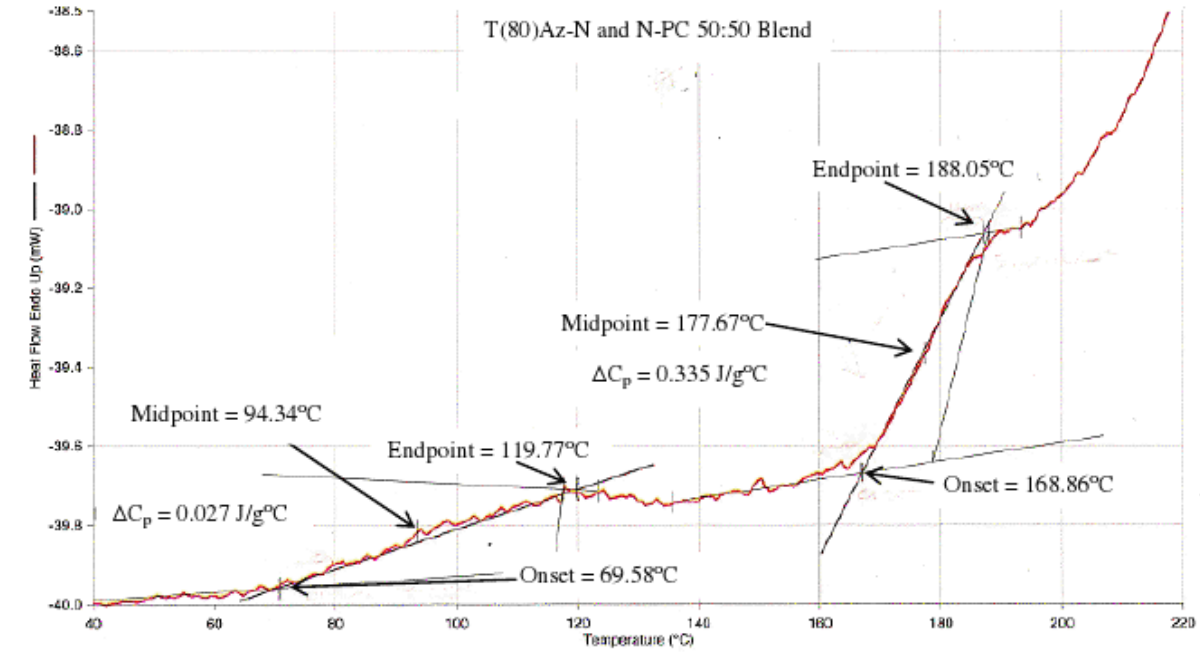


Figure 34. DSC Scan of T(80)Az-N and N-PC 50:50 Blend

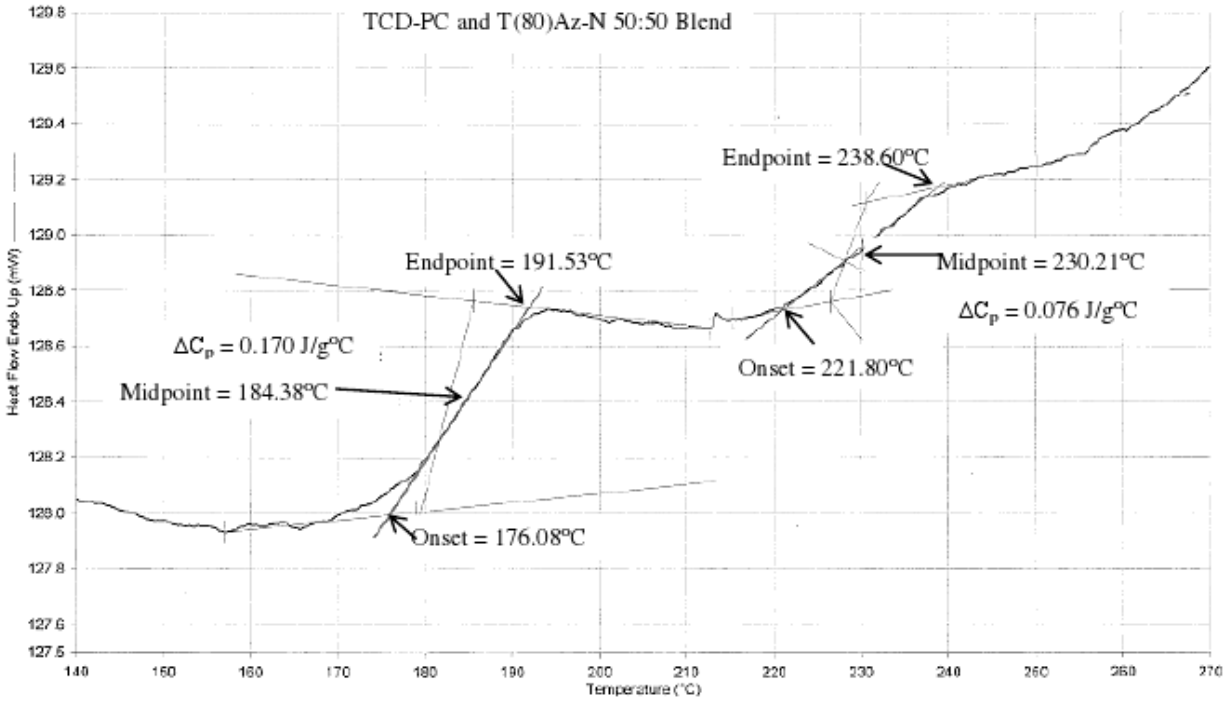


Figure 35. DSC Scan of TCD-PC and T(80)Az-N 50:50 Blend

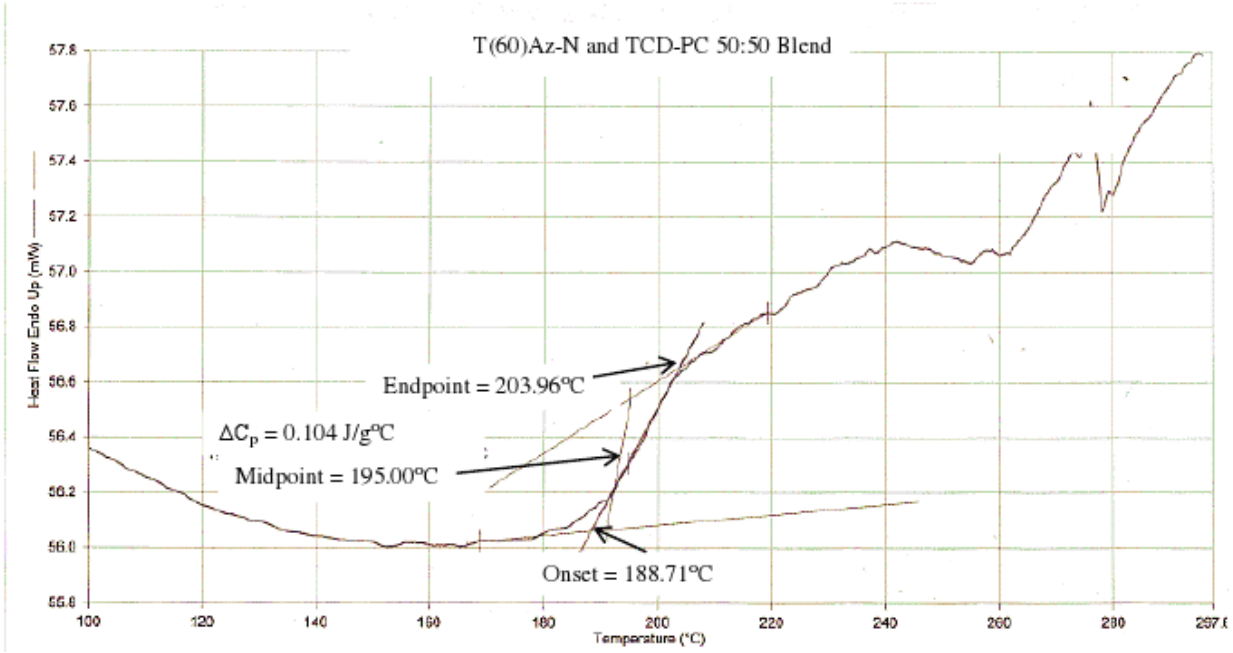


Figure 36. DSC Scan of T(60)Az-N and TCD-PC 50:50 Blend

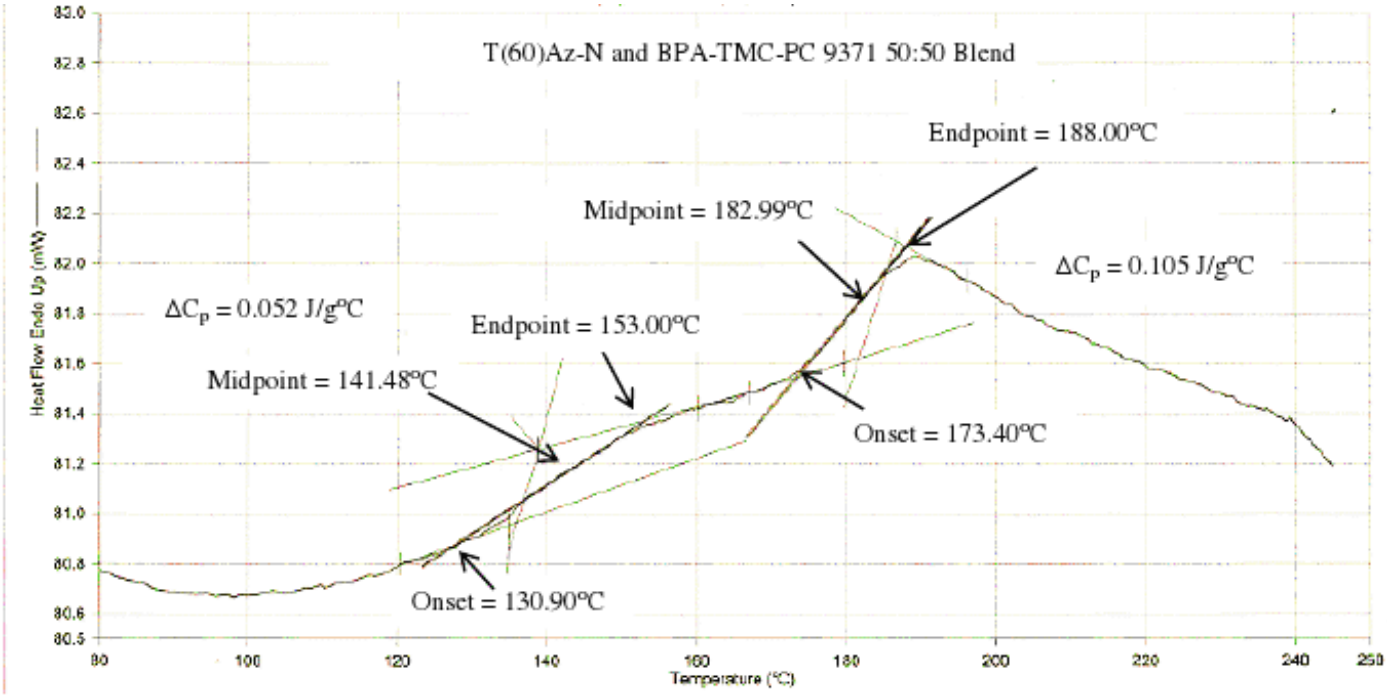


Figure 37. DSC Scan of T(60)Az-N and BPA-TMC-PC 9371 50:50 Blend

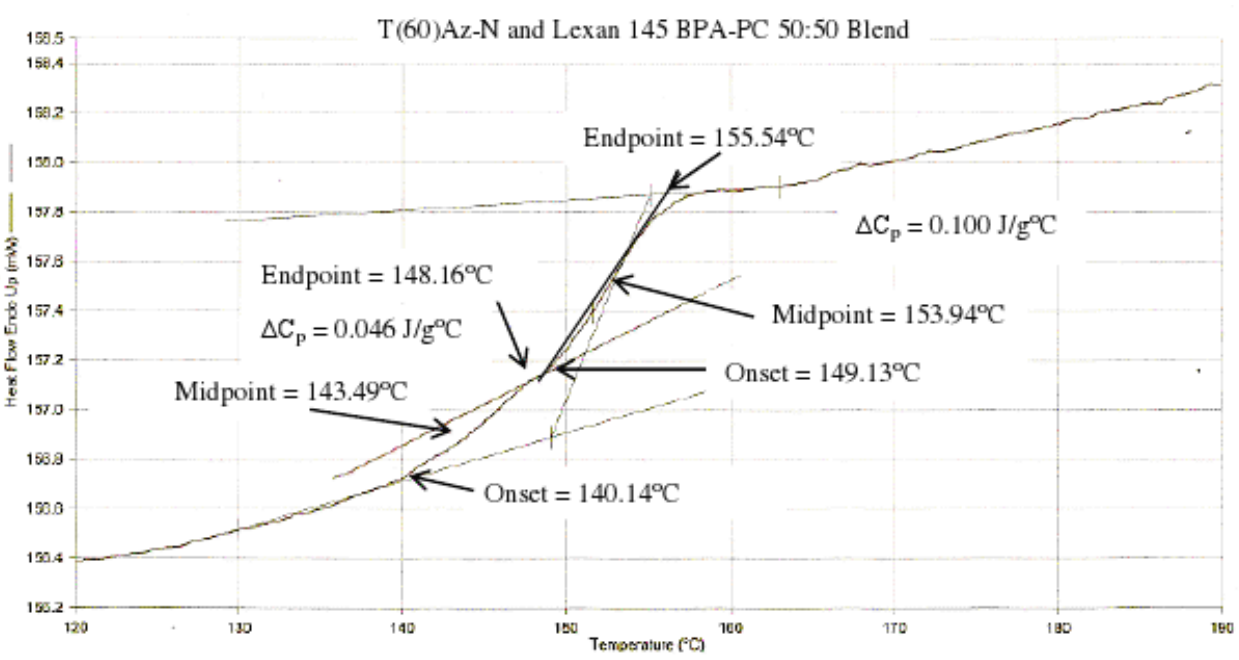


Figure 38. DSC Scan of T(60)Az-N and Lexan 145 BPA-PC 50:50 Blend

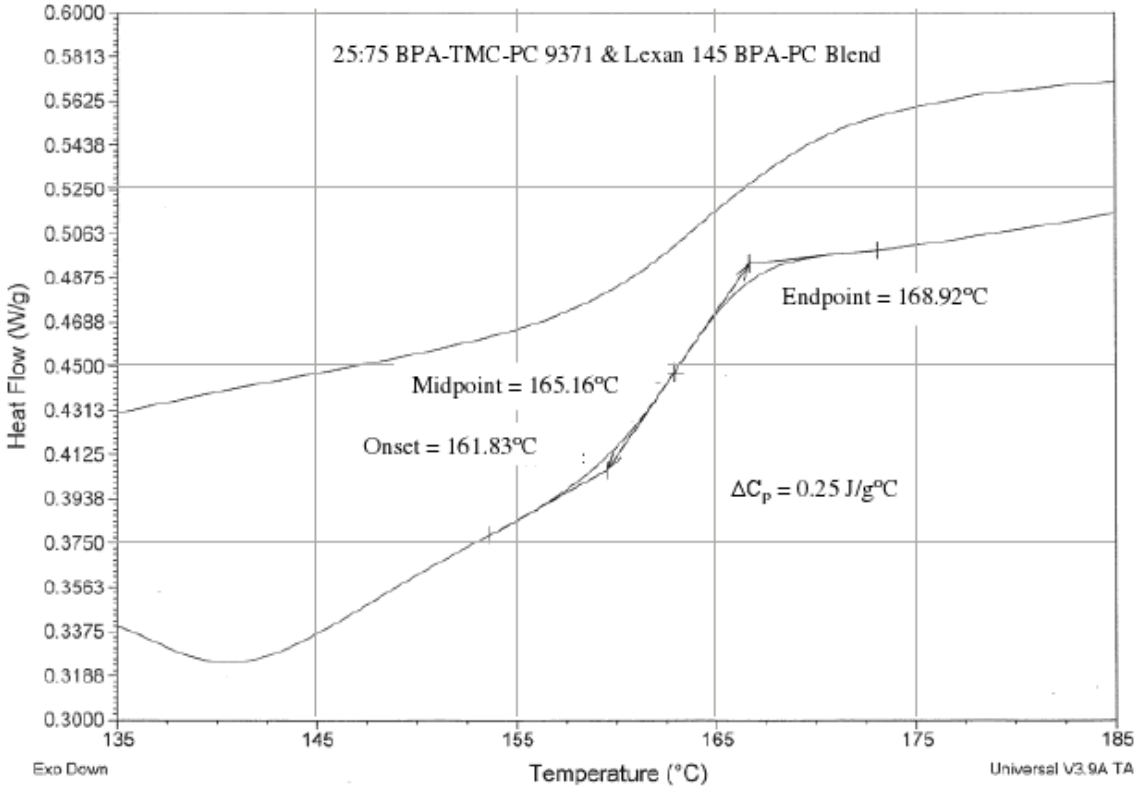


Figure 39. DSC Scan of 25:75 BPA-TMC-PC 9371 and Lexan 145 BPA-PC Blend

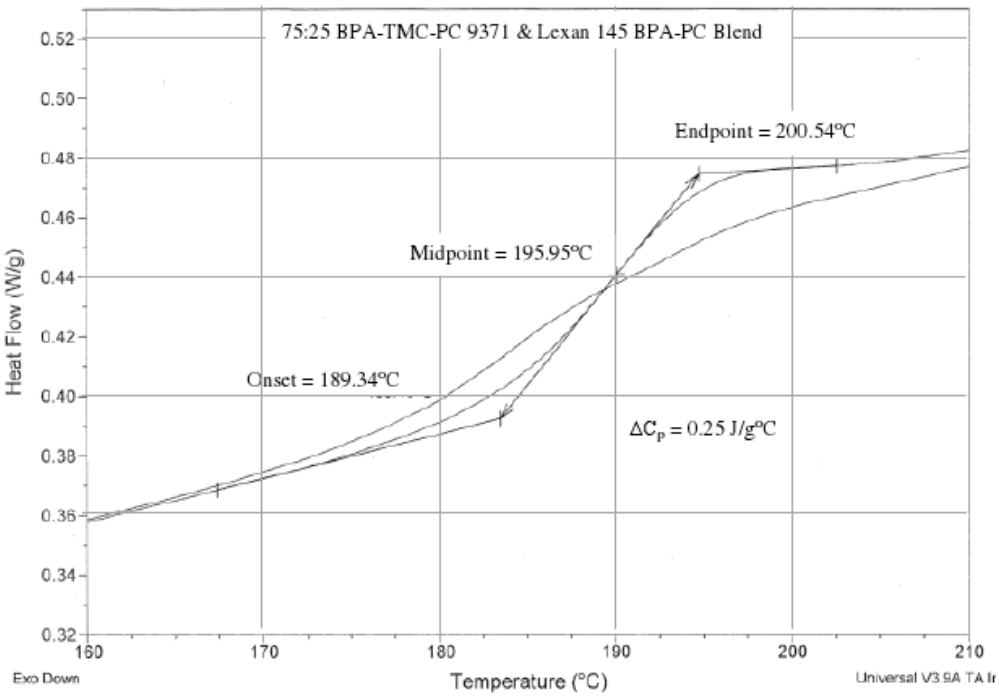


Figure 40. DSC Scan of 75:25 BPA-TMC-PC 9371 and Lexan 145 BPA-PC Blend

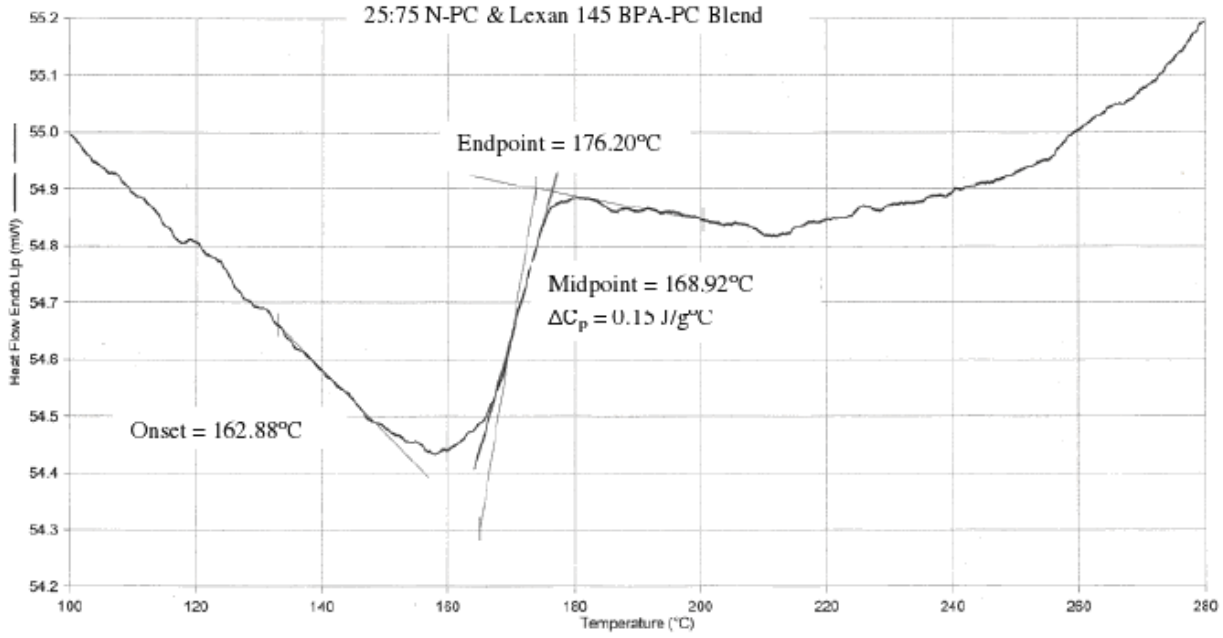


Figure 41. DSC Scan of 25:75 N-PC and Lexan 145 BPA-PC Blend

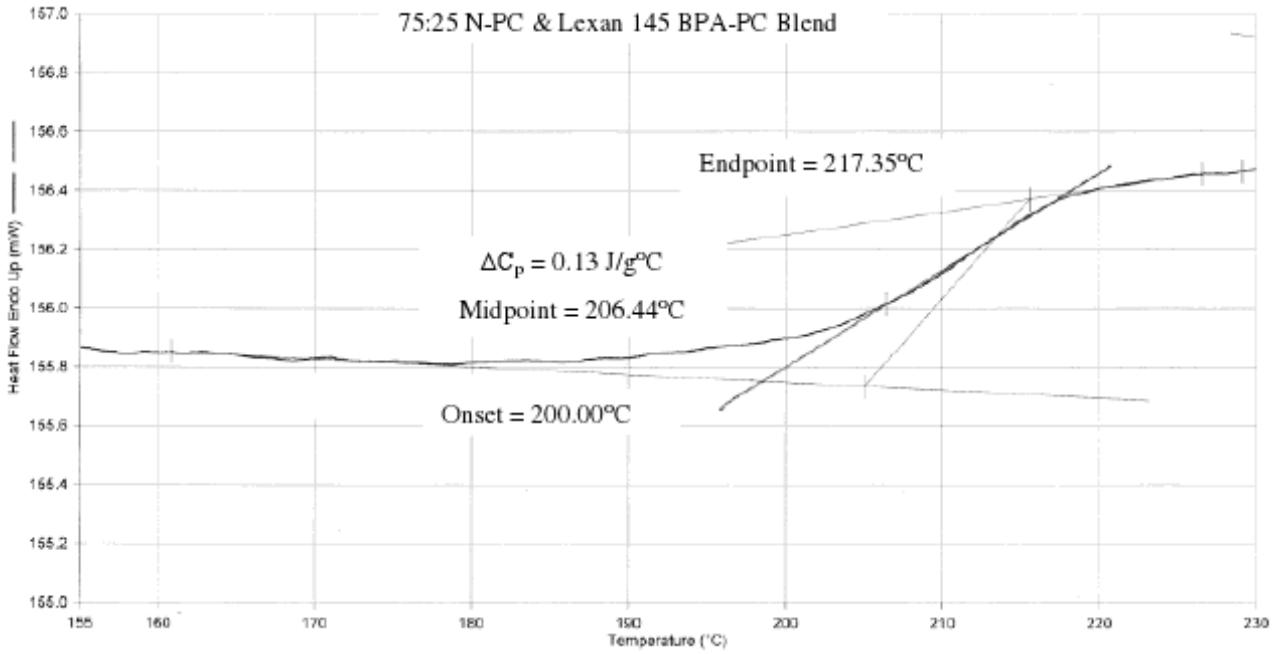


Figure 42. DSC Scan of 75:25 N-PC and Lexan 145 BPA-PC Blend

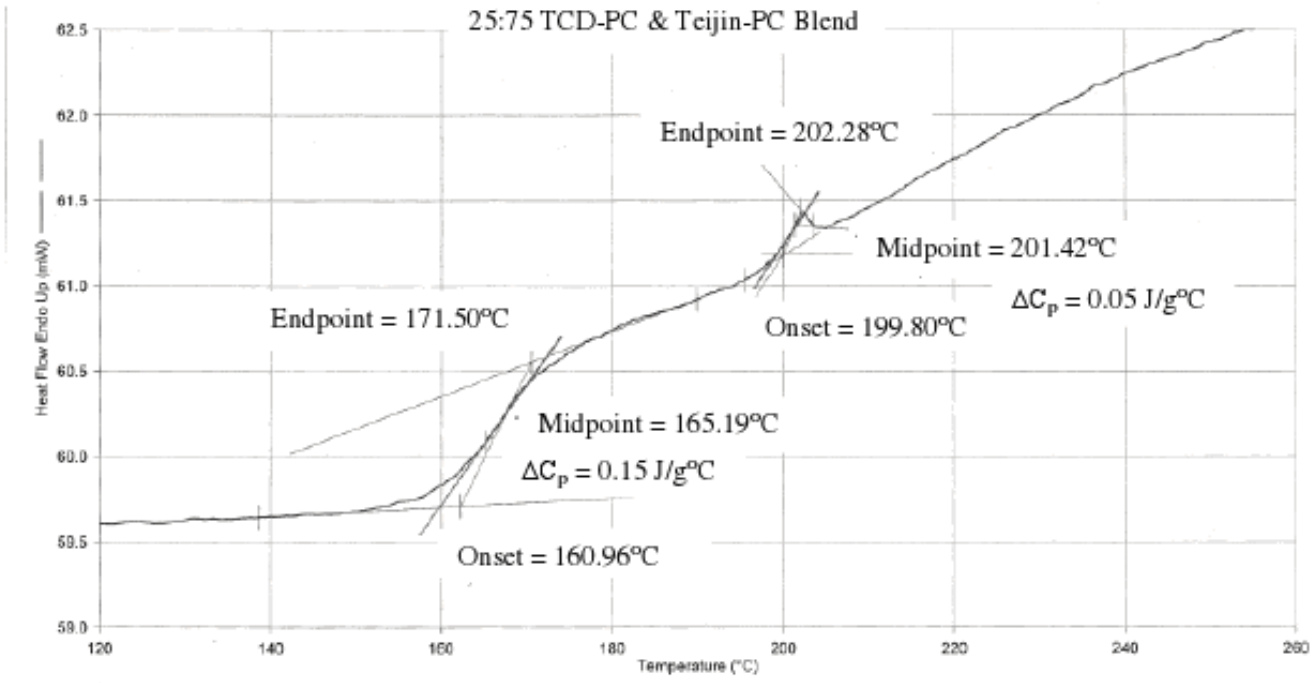


Figure 43. DSC Scan of 25:75 TCD-PC and Teijin-PC Blend

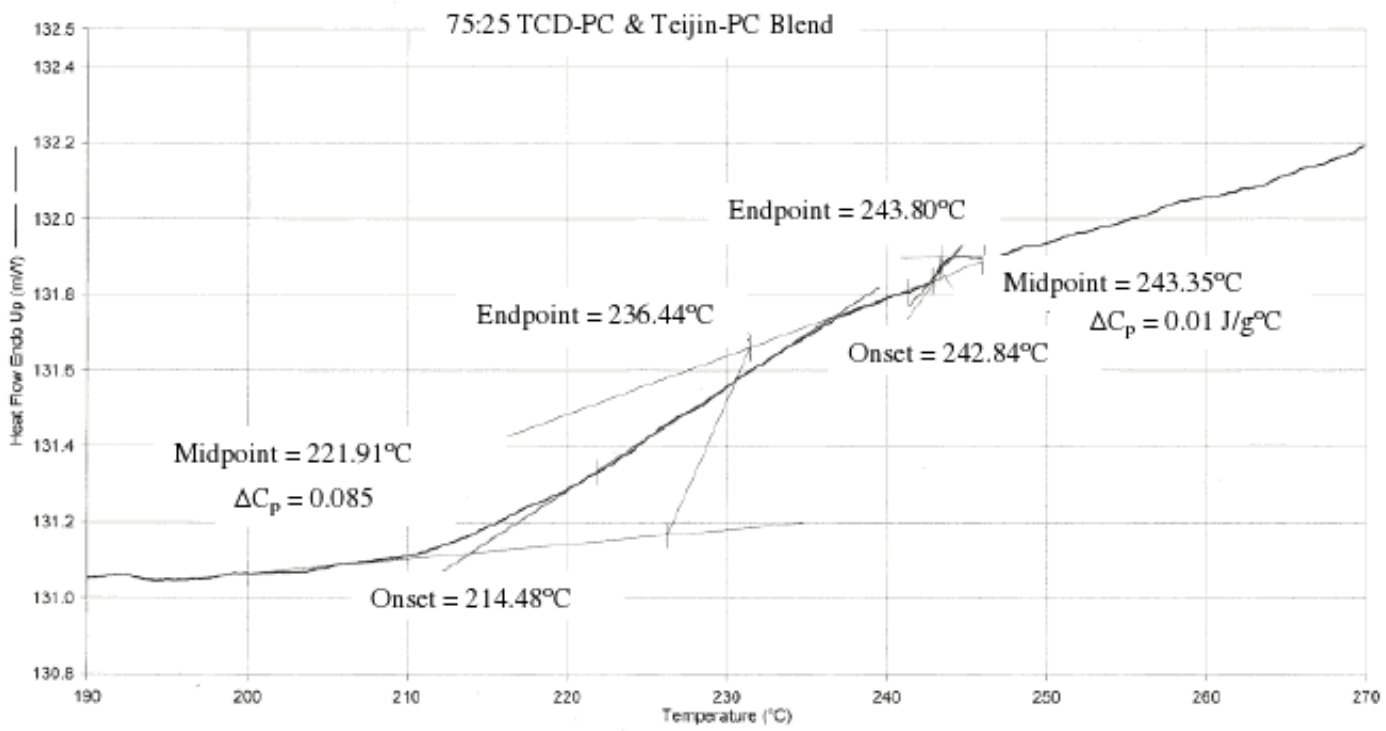


Figure 44. DSC Scan of 75:25 TCD-PC and Teijin-PC Blend

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